THE PHYSICAL STRUCTURE OF BUTTER AS AFFECTED BY NEWER MANUFACTURING PROCESSES.

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J. M. de Man

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THE PHYSICAL STRUCTURE OF BUTTER AS AFFECTED BY NEWER MANUFACTURING PROCESSES

A DISSERTATION
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

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by
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ABSTRACT

Physical properties and structure of butter are greatly influenced by the manufacturing technique. By the use of polarized light microscopy continuously made butter was found to have a continuous fat phase and a disperse phase of fat crystals and serum droplets. The fat crystals in conventional butter were smaller and the disperse phase included also fat globules and gas bubbles. The former butter type was much harder than the latter at any season but both types exhibited similar seasonal hardness variations. The characteristic crystal structure and low gas content of continuously made butter are factors causing the hardness differences of the two butter types.

The setting (hardness increase after manufacture) characteristics of the two butter types were different largely because of continuing crystallization in the continuously made butter. In conventional butter there were thixotropic changes but no continuing crystallization. Thixotropy in both types was influenced by initial hardness and probably depended on the content of very small fat crystals.

The higher oiling-off tendency of continuously made butter is explained by the absence of globular fat and a lower melting point of the solid fat phase as a result of mixed crystal formation.

The rapid cooling of pure butterfat increased the ratio of solid to liquid fat as shown by dilatometry and concurrently the melting point was lowered. Considerable seasonal differences in solid fat content of butterfats were demonstrated by this technique. Rapidly cooled butterfat required more heat, measured calorimetrically, to melt than slowly cooled butterfat at the same temperature. For unknown reasons seasonal differences in the crystalline fat content of butterfat could not be detected by calorimetry.

ACKNOWLEDGEMENTS

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THE PHYSICAL STRUCTURE OF BUTTER AS AFFECTED BY NEWER MANUFACTURING PROCESSES

INTRODUCTION

There is a widespread trend towards rationalization of methods in modern industry and the word automation is usually connected with this trend. Evidence for this tendency is the change from batch processes to more efficient continuous methods of production. The dairy industry has been no exception to this general rule. The oldest and best example is the continuous pasteurization of milk, which has now to a large extent replaced the older vat-pasteurization method. This new process, called HTST (for high temperature, short time) pasteurization, employs plate heat exchangers for a continuous heat treatment of milk. Ice-cream was the next product to be affected by automation. Continuous ice-cream freezers were developed and their use has probably contributed to the development of continuous butter making equipment. Cheese making is the only main branch of dairy manufacturing in which the introduction of continuous methods still encounters

serious difficulties. There is not as yet any cheese made commercially by a continuous method.

Buttermaking, which was traditionally done in churns, was the most recent procedure to be adapted to continuous methods. Considerable effort has been expended toward perfecting such continuous processes, several of which are now in commercial use. They are of two general types, those developed in Europe, in which butter is made from cream directly, and those developed in the United States, in which butter is made from butterfat that has first been separated in the form of butteroil from the cream.

The introduction of these new methods, however, has also created new problems, and, on the occasion of the first Canadian installation of a continuous buttermaking unit, the Canada Department of Agriculture invited the Department of Dairying, University of Alberta, to conduct a study of this new process. The following is an account of part of the results obtained during the course of this work.

REVIEW OF LITERATURE

General

The physical structure of butter - the manner in which its components are distributed, intermingled and linked together - is intimately connected with the mechanism of the churning and working processes (7, 41, 43, 71, 94). In addition, the important physical properties, e.g. spreadability, are mainly, if not completely, determined by the particular structure of a butter (44, 73).

The physical structure of conventional (churned) butter has received considerable study and much effort has been expended towards influencing the physical structure in such a way as to obtain butter with more desirable physical properties (1, 3, 19, 32, 46, 63, 65, 66, 79, 80, 109, 110, 111). The use of continuous manufacturing methods, in which fundamentally different procedures and treatments are employed, will undoubtedly profoundly affect structure and properties of the resulting butter.

A study of the physical structure of continuously

made butter cannot be made without a consideration of the available information pertaining to conventional butter and, therefore, this review will consist of a survey of the literature on structure and properties of conventional butter, followed by an account of the meagre literature on continuously made butter.

Conventional butter

Theories of butter structure. Several theories have attempted to explain the complicated disperse system of butter. Originally (43) butter was considered simply as a structureless mass. After Storch in 1897 established the presence of fat globules in the fat phase of butter the theory was advanced that butter is a fat in water system, which is directly opposite to the older concept (43). According to this theory, butter is a system of fat globules interwoven by a continuous network of hydrated fat globule membranes, while the water droplets are interspersed between the fat globules and connected with each other by means of the membrane network.

It was King (37, 38) who expressed the opinion that the presence of fat globules can be reconciled with the existence of a continuous fat phase. According to his idea the fat in butter occurs in two forms, as

globules and as free fat, the last form originating partly from the fat squeezed out from the globules and partly from the crushed globules. The free fat constitutes the continuous phase and in it are embedded the fat globules (39) and moisture droplets. This viewpoint was corroborated by the fact that butter can be "diluted" with the continuous phase - a liquid fraction of butterfat - and by the easy diffusion of fat soluble dyes into the butter (37). King was the first to consider the importance of segregation of milk fat into a liquid and a crystalline portion during the churning process. Measurements of the dielectric constant of butter by Mohr and Hennings (60) indicate a nearly complete inversion of phases. The dielectric constant for cream was about 130, for butter between 5 and 7.5, which is close to the value for pure butterfat, 3. The theory of King has been extended by others (62, 73) and it is assumed that liquid fat is liberated from the fat globules during churning and serves as a cementing medium for them in the butter granules. The older theory of Rahn has to a certain extent been revived recently (72). It is claimed that butter may simultaneously possess two continuous phases - fatty and aqueous. According to this point of view, the fat globules, with their hydrated

membranes, and the moisture droplets, lie so close to each other that a continuous network of water canals is formed. With the close proximity of various particles in butter it is very likely that some connection exists between various water particles. The ideas of King concerning the structure of butter are now generally accepted. According to this point of view butter is a disperse system with liquid fat as the continuous phase in which are dispersed fat globules, fat crystals, serum droplets and air bubbles.

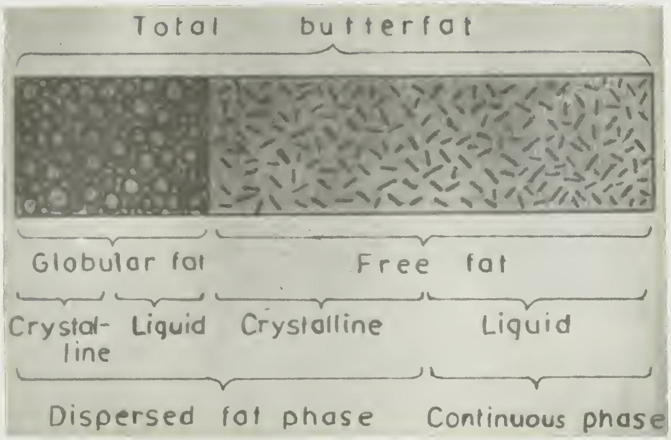
Factors influencing butter structure. According to Mulder (73) the physical structure of butter is influenced by the following factors:-

1. The structure of the materials from which the butter is prepared.
2. The method by which the butter is made.
3. The treatment of the butter after its preparation.

The structure of the materials is important because the main component of butter, the fat, occurs in dispersed form in the milk. The fat droplets are protected from coalescence by a complex membrane, which consists in large part of protein (40, 45).

Some of these fat globules are carried over into the butter with their protective membranes intact. At body temperature the fat is completely liquid but at lower temperatures the fat is a mixture of solid and liquid components. Only at very low temperatures, -30°C. or lower, is butterfat completely solid (24). Butter owes its characteristic plasticity probably entirely to the presence of fat in crystallized form. The different forms in which the fat is present in butter has been schematically represented by King (43) as shown in fig. 1.

Fig. 1. Forms of butterfat in butter after King.



It has been claimed that the presence of fat globules in butter influences its consistency and

spreadability (63). Cream is cooled many hours before churning, and crystallization of the fat in the globules is practically complete after churning. As all crystallization takes place inside the globules, the individual fat crystals are consequently limited in size. The fat crystals in the free fat have been reported to be as small as 0.1 μ (106). Crystals of such small size are no longer visible in the polarizing microscope (47), which may explain why rapidly cooled butterfat was claimed (62, 70) to contain no crystals and to exist in a gel form.

Fat is the most variable constituent of milk both quantitatively and qualitatively. The chemical composition of milk fat is subject to considerable seasonal variation. Reports (11, 26, 53, 55, 91, 101) are available from different countries showing wide seasonal differences in the proportions of unsaturated and short chain fatty acids. Chemical and physical constants of Alberta butterfat (113, 114) were determined as an indispensable introduction to the work reported herein. It has been stated that the consistency of butter is mainly determined by the condition of the fat in it (70). The large differences in unsaturation and chain length of the fatty acids in

butterfat result in a high hardness of winter butter as compared with summer butter (10, 66). The hardness and consistency of butter depend on the ratio and composition of the liquid and crystalline forms of the fat (17, 51). Dilatometric measurements on cream showed that more fat crystallized in winter than in summer cream, when compared at the same temperature (2, 76, 93). Thus, there is little doubt that the proportion of solid to liquid fat is a factor determining butter hardness.

In addition to the fat, which is the main constituent, butter contains moisture in the form of small droplets ranging in size from 1-50 μ (44, 48, 78, 95). The quantity of moisture in Canadian butter is legally prescribed to be not over 16.0%. There is, therefore, very little variation in water content of different butters made in this country. All conventional butters also contain gas in varying quantities. Values have been reported as high as 14.0% (54) but the average seems to be from 3-5% (105). It is claimed that size and number of gas bubbles in butter influence its properties, notably oiling-off (58) and hardness (64). The influence of gas on butter structure and properties has been very difficult to investigate because in the conventional buttermaking methods there was no

possibility of consistently controlling the gas content of the butter. The introduction of vacuum churns made possible the production of butter under reduced pressure with resulting low gas content. Some reports of investigations made in this way indicate that the presence of gas lowered butter hardness (83, 104, 116) but in some other studies no measurable differences were found (33, 102).

The method by which butter is made may profoundly influence its physical structure (41). The work done on this subject has been exclusively concerned with conventional butter. It has long been known that variations in cooling treatment of cream may influence physical structure and consequently properties, especially firmness, of butter (1, 3, 19, 46, 63, 65, 66, 79, 80, 109, 110, 111). A well known method is the one developed in Sweden by Samuelsson and Pettersson (46). Since its development in 1937 it has found widespread application in Scandinavia and Germany (64). The method is claimed to influence butter properties by its effect on the quantity of crystalline fat as well as on the way fat crystals interlock, rather than by its effect on crystal form (63). While this method was developed for the production of

cultured cream butter, other methods suitable for sweet cream butter production were advocated (9, 11). Coulter and Combs (9) concluded that butter hardness is increased by the following factors: cooling of the cream to a low temperature, rapid cooling of the cream to below 40°F., churning at a low temperature; these authors also found that lower temperatures of the wash water gave softer butters. This work was preceded by a study of the relation between the hardness of butter and the iodine number of the butterfat (8). It could be shown that a relation existed between seasonal fluctuations of iodine number and hardness of the butterfat. Wilster et al. (109, 111) found that churning cream immediately after pasteurization and cooling resulted in a hard butter. Cooling of cream, after pasteurization, to 50°F. and holding overnight resulted in a softer butter. These authors called their procedure the 50-45-40 method and it was claimed to improve the texture of fall-and winter-made butter. The improvement was effected by suitable temperature treatment of the cream. Storage temperature of the finished butter was also indicated to influence butter texture . In a later paper (110) Wilster describes in detail a method that will result in easily spreadable

butter. This method appears to be identical with the one developed earlier by Samuelsson and Pettersson (46). No attempts were made to explain the resulting differences in properties in terms of changes in physical structure. Adriani and Tamsma (3) conclude that softer butter will result when: (a) the structure leading to brittleness is destroyed, and (b) the percentage of crystallized fat in butter at a given temperature is as low as possible. Mulder (69, 74) pointed out that hardness measurements made shortly after manufacture of butter are unreliable because subsequent changes in hardness may occur to a different extent in different butters. Mulder (70) found that the use of cream cooled to low temperatures resulted in hard butter. An explanation of this phenomenon is given in terms of butterfat crystallization.

No increase in the hardness of summer butter was obtained by Adriani and Tamsma (1) with variations in temperature treatments. Olsson (79) showed that cream cooled after ripening gives harder butter than cream cooled before ripening. It was also found that the churning temperature does not have any influence on the consistency of the butter. In an investigation by Dolby (16) on the effect of type of pasteurizer, rate of cooling after pasteurization, temperature during holding and churning, temperature of wash water and amount of

working, it was shown that of these factors the only one which had any marked and consistent effect on the hardness of the butter was the rate of cooling of cream after pasteurization, rapidly cooled cream yielding harder butter. The use of low temperature wash water tended to reduce the hardness of butter but the effect was small. The other factors had no consistent effect on the hardness of the butter. The same author later (18) concluded that more uniform consistency of butter throughout the season could be achieved only by reducing the hardness of the firmer butter and not by increasing the firmness of the softer butter. He also found that slowly cooled cream yielded a softer butter than rapidly cooled cream. Mohr and von Drachenfels (65) found that to obtain a summer butter of sufficient firmness it was necessary to keep temperatures of cream, butter granules and butter wash water at a low value. The authors claim that the formation of fat crystal nuclei is greater at lower temperatures. They also mention the possibility of formation of mixed crystals.

It appears from the foregoing that a number of factors may be important in influencing properties and structure of butter. Some of these are: speed or rate of the cooling of the cream, temperature to which the

cream is cooled, holding temperature, temperature of butter wash water (105), and temperature of salt added to the butter in the churn (110). Despite the voluminous literature on this subject there remain many unsolved problems. While it is stated that agreement exists that winter cream should be cooled slowly to obtain softer butter (105), other sources indicate that the speed of cooling is without effect and that only the final temperature of the cream determines the butter hardness (46). Dolby (17), from a study of a large number of butters, concluded that only a small part of the variation in hardness was due to manufacturing variations, and that at least 80% of the variation could be attributed to differences in the raw material.

The treatment of butter after its preparation has often been overlooked as a factor influencing its physical structure. Nevertheless, several authors have called attention to changes occurring in the finished butter and their influence on its properties (56, 66, 69, 74, 85). An indication of the changes in physical structure that may take place in butter subsequent to manufacture is the increase in hardness that usually occurs, a phenomemon called setting. According to Mulder (69) a twenty-fold increase in

hardness may occur. While this figure seems high, considerable hardness increases during setting have been reported by other workers (74, 85).

Two factors have been proposed to be responsible for the hardening effect: (a) the completion of unfinished and retarded crystallization, and (b) thixotropic changes. Continued crystallization increases the proportion of solid to liquid fat, whereas thixotropy involves changes in spatial arrangement of the dispersed particles. Some investigators infer that setting is solely caused by continued crystallization (13, 63, 100), but Mulder (69) points to the importance of thixotropy in the setting process. The hardening effect is usually measured in butter stored at lower than manufacturing temperature so that crystallization could be a factor but it has also been shown (102) that the hardness increased when butter was held at a temperature higher than the churning temperature, which is an indication that continued crystallization cannot be the only cause of the setting effect.

Thixotropy occurs in colloidal dispersions and is defined as a reversible, isothermal, sol-gel transformation (12, 20). It has been shown that thixotropy

involves the formation of a structure of the scaffolding type by the dispersed particles (21). This requires the presence of attractive forces between the particles (29) for which van der Waals' forces are assumed to be responsible. In an undisturbed dispersion the particles arrange themselves in such a way as to form a continuous structure whereby the system acquires solid properties. On the application of a shearing stress, links between the particles are broken and a much lower resistance to deformation results. It has been found that the working of butter that had been allowed to set decreased its hardness and that on subsequent storage hardness again increased, but never regained the original value (66, 85).

Continuously made butter

Physical structure and properties of butter made by the continuous process most widely used on the North American continent* have received very little study. Weinreich (107) in a general description of the method stated that continuously made butter had a closer texture and finer body than the churn-made product. For equal quantities of salt and colour added the resulting

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* A method developed by the Cherry-Burrell Company of Cedar Rapids, Iowa.

flavour was stated to be more bland and the colour lighter. According to Weinreich (107) considerable interest has been manifested in the difference in crystalline structure of butters made by the new and the old processes. He stated that on the basis of his own observations no conclusions could be reached. It was observed, however, that the fat crystals in churn-made butter change considerably the first few days after manufacture, and that well chilled churn-made butter has considerable resemblance to Cherry-Burrell butter as far as crystalline structure is concerned. It was remarked that detailed studies on this subject had as yet not been made. In a paper (52) describing the installation of a continuous buttermaking unit it was stated that the texture problem presented the biggest difficulty. In a book on continuous buttermaking (108) it is held probable that in the Cherry-Burrell buttermaking method a product is obtained in which the milk serum as well as part of the butterfat is present as continuous phase. According to these authors it is not known with certainty whether the Cherry-Burrell product has the fault of oiling-off. According to King (42) the Cherry-Burrell butter contains only very few fat globules, and the fat crystals are in the form of small needles with a size

of 3 - 5 microns, occasionally up to 15 microns. The same author states that this butter has a coarse moisture dispersion causing it to have a deep colour. Elsewhere, King (41) remarks that in the Cherry-Burrell process the thixotropic changes seem to occur mainly in the texturator.

METHODS

Polarized light microscopy. As it was desirable not only to obtain information on size and shape of fat crystals but also on their approximate quantity, a technique was developed which made it possible to examine layers of butter of definite and known thickness. As the butter at the temperature of examination (5 - 10°C.) is too hard to be easily spread on a glass slide, a dilution method was necessary. This gives the added advantage of more detailed pictures.

A definite quantity of butter was weighed on a slide. The weight of the sample was calculated so that it would form a layer 10 microns thick when spread evenly over the area occupied by a round cover glass of 22 mm diameter. An equal quantity of light mineral oil was then weighed on to the same slide and the two substances mixed carefully and thoroughly with a small spatula. Because some of the specimen adheres to the spatula, the slide was weighed again and the weight of specimen reduced to half by removing

the excess with the spatula. When covered with the round cover glass and spread evenly with slight pressure to fill exactly the area under the cover glass, this quantity of specimen yielded a layer 10 microns thick, representing half butter and half mineral oil.

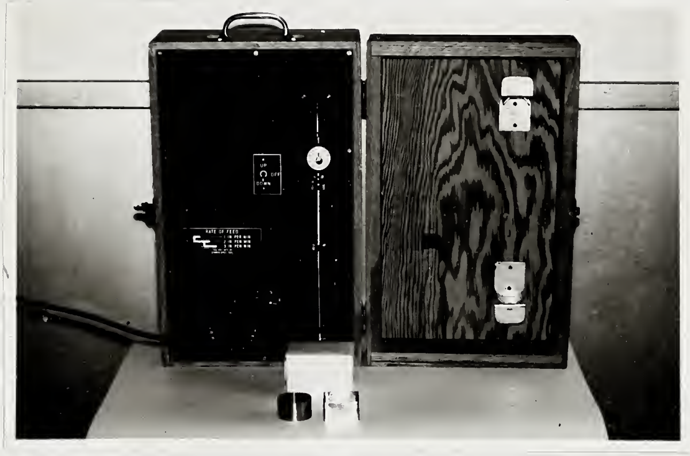
The microscope used in this study was a Zeiss-Winkel standard polarizing microscope which has the illumination built into the base. The photomicrographs were made with the Zeiss-Winkel attachment camera and focusing eyepiece. The magnification on all photographs is 750 x.

Moisture distribution. The size distribution of moisture droplets was measured by the method described by Rahn and Boysen (89). The moisture droplets were measured and counted directly in a thin film of butter under the microscope at a magnification of 900 x. The microscope was fitted with an ocular micrometer divided into 100 squares of 144 μ^2 surface area each. Two preparations were made from each sample and four countings from each preparation. The droplets were divided into groups, the first comprising all of those up to 3 µ in diameter, the next from 3 - 5 µ, then 5 - 10 µ,

10 - 15 μ and 15 - 25 μ. The droplets of group 1 were counted in 16 squares, all other droplets in 100 squares. The results are expressed as the percentage of the total volume occupied by the droplets of each group. The reporting of the droplets as percentage of the total number of droplets would overemphasize those in the lower size range.

Hardness. Butter hardness is usually measured in the range of 12-17°C. and in choosing measurement temperatures the important consideration is that the range of hardness values encountered falls within the range of the particular instrument used. In this investigation all samples could be measured by the penetrometer method at 17°C. and by the sectility method at 12°C. In the penetrometer method, a modification of the procedure described by Kruisheer and den Herder (50), a specially designed plunger is driven down into the butter at constant speed (5 cm/min.) and the resistance to deformation registered on the gauge. The plunger is allowed to penetrate 1 cm into the butter after which the maximum reading is recorded. The plunger has a surface area of 4 cm^2. The instrument is calibrated with a balance and gauge readings are converted to

Fig. 2. Apparatus for the measurement of butter hardness.



Kg/$4cm^2$ with the aid of a standard curve. Each butter sample was prepared for hardness measurement, immediately after manufacture, by being pressed into a square frame of 5 cm side and 2.0 cm height fabricated from 20 gauge stainless steel sheet. For certain experiments it was necessary to use continuous type butter made with the experimental continuous buttermaking machine (115), and for this purpose the butter was extruded directly into round frames consisting of 2.9 cm lengths of 2 in. O.D. stainless steel tubing. The sectility method differed from the

penetrometer method in that the plunger was replaced by a taut stainless steel wire (diam. 0.015 in.) held in a frame. The gauge reading was taken when the wire had travelled 2.5 cm through a block of butter 5 cm wide which had been pushed from one of the square stainless steel frames described above.

The butter samples unless otherwise stated, were kept in the frames in a cold storage room at 5°C. for 1 week, and then tempered in a water bath for 24 hours prior to testing. Water bath temperatures of 17°C. in the penetrometer method and 12°C. in the sectility method were maintained thermostatically within ± 0.05°C. and measurements in a room having a temperature of 5-10°C. immediately followed removal of samples from the water bath.

Each hardness value, unless otherwise specified, is the average of two determinations. Penetrometer hardness is expressed as Kg/4 cm^2, whereas sectility is expressed as Kg/5 cm, since 5 cm was the length of the wire in contact with the butter.

To test the accuracy of the methods, ten replicate samples of continuously made, and ten of conventional, butter were measured by both penetrometer

and sectility methods. From the results (table 1), it appears that the accuracy of the methods is very satisfactory.

Round frames gave very slightly higher penetrometer hardness than square frames when the butter was hard, but not when the butter was soft (table 2).

Oiling-off The method used was similar to the one described by Mohr and Baur (58). Cubes of butter were stored on a pile of filter papers for 48 hours at 25°C. As it is difficult to cut perfect cubes with a stretched wire a special forming device or trier with a 2.5 by 2.5 cm internal cross section was fabricated from stainless steel sheet. When pushed into the butter at 5°C. and withdrawn, this trier removed a plug of butter of similar cross section. The butter was pushed out of the trier by a closely fitting plunger with an attached graduated stem and the plug was cut with a stretched wire at the 2.5 cm length.

The cube of butter was placed on a pile of ten Whatman No. 1 filter paper circles of 12.5 cm diameter and of known weight. The papers and butter cube were weighed and stored at 25°C. for 48 hours and the

TABLE 1. The accuracy of hardness measurements

	Conventional		Continuous	
	Penetrom.	Sect.	Penetrom.	Sect.
Range*	2.00-2.12	0.24-0.26	3.94-4.14	1.02-1.08
Mean	2.05	0.25	4.05	1.05
Av. Dev. from Mean	±1.5%	±4.0%	±1.4%	±2.1%

*10 replicate samples of each type of butter

Table 2. The influence of shape of frames on butter hardness values

Description of Sample	Penetrometer Hardness Kg/4 cm^2	
	Round Frames	Square Frames
Hard Butter*	2.40	2.20
Soft Butter*	0.84	0.84

*Average of 4 samples each

cube then removed. During the storage period the filter papers may absorb some moisture from the atmosphere. To serve as a control, a pile of ten similar filter papers without a butter cube was stored under the same conditions. After removal from storage these and the papers with the absorbed oil were held in a dry atmosphere until the control returned to its original weight. The papers with the absorbed oil were held in a dry atmosphere until the control returned to its original weight. The papers with the absorbed oil were then weighed. Oiling-off is expressed as the weight increase of the filter papers in terms of percentage of the weight of the original butter cube.

Gas content. A direct method was used in which the gas was liberated from the butter by melting. The escaping gas was collected under water in a graduated tube. The apparatus consisted of brass cones of the following specifications: height 44 mm, small inside diameter 22 mm, large inside diameter 28 mm, capacity approximately 20 g; glass funnels (diam. 7 cm) with stems cut to a length of 1 cm; graduated tubes, fabricated from 5 ml measuring pipettes, capacity 2 ml, closed at one end; rubber connection tubes, length 1 cm.

The funnels with the graduated tubes disconnected

were placed in liter beakers filled with water. The air was then expelled by boiling the water and the whole was subsequently cooled to room temperature. Without removal from the water the water-filled tubes were fitted to the stems of the inverted funnels by means of forceps. To avoid excessive foaming a few drops of sodium hexadecylsulfate were added to the water. The weighed cones were pressed base first into the butter, which had been tempered at 15°C. in an incubator. The ends were carefully wiped clean and the filled cones weighed. These were then immersed in the beakers underneath the funnels. The contents of the beakers were heated to 50°C. and the collected gas in the graduated tubes read after cooling to room temperature. Volume was converted to standard pressure (760 mm Hg) and expressed as ml per 100 grams of butter.

Dilatometry. The dilatometers were of the volumetric type with a capacity of approximately 10 ml and a stem calibrated in mm^3. The confining fluid was dye-colored water which was boiled and cooled before use. Butterfat was prepared from butters of minimum, intermediate, and maximum hardness, obtained in June, September and December respectively. The pure fat was prepared by the melting, centrifuging and filtering of butter. Before transfer to

the dilatometers the filtered fat was dried and deaerated in roundbottom flasks under reduced pressure (5-10 mm Hg) for at least 30 minutes at 90°C. with occasional violent shaking. The dilatometers were weighed before and after filling to obtain the weight of the fat by difference. Two grams of confining fluid were used in all measurements.

The percentages of liquid and solid fat in a mixture may be calculated from knowledge of the thermal expansions of the fat when liquid and solid. The thermal expansion of completely liquid butterfat, measured between 40 and 60°C., was 8.5 $mm^3/10g.°C$. The measurements on completely solid fat were made between -50 and -40°C. and the thermal expansion found to be 5.8 $mm^3/10g.°C$. For these latter measurements a special confining fluid had to be used which consisted of a concentrated alcoholic solution of either calcium chloride or potassium acetate. The thermal expansion of these confining fluids was determined separately. Melting started in all the butterfat samples at about -35°C., and about 20-30% of the butterfat was liquid at 0°C. the percentage varying with season. This confirms a recent report (24) in which the earlier idea that butterfat would be practically completely solidified at 0°C. (75)

was disproved. The values obtained in the above measurements are the average of at least six determinations and in their calculation corrections were applied for the expansion of the glass.

When the thermal expansions are represented graphically as in fig. 3, the melting dilation at any one temperature is equal to the distance between the curves at that temperature (e.g. ab in fig. 1 represents the melting dilation at 20°C.). The melting dilations, i.e. the expansion values for complete isothermal change from solid to liquid, for the temperatures at which measurements were made are listed in table 3.

When the reading for the completely liquid fat is made at 40°C., the melting expansion D_t is calculated as follows:-

$$D_t = \frac{10}{w} (R_{40} - R_t - EW_t) - M_{40,t}$$

where w = weight of butterfat; R_{40}, R_t = readings of dilatometer at 40°C. and t°C. respectively; EW_t = thermal expansion of 2 g of water between t° and 40°C.; and $M_{40,t}$ = thermal expansion of 10 g of fat between t° and 40°. The values for the thermal expansion of water were obtained from the International Critical Tables.

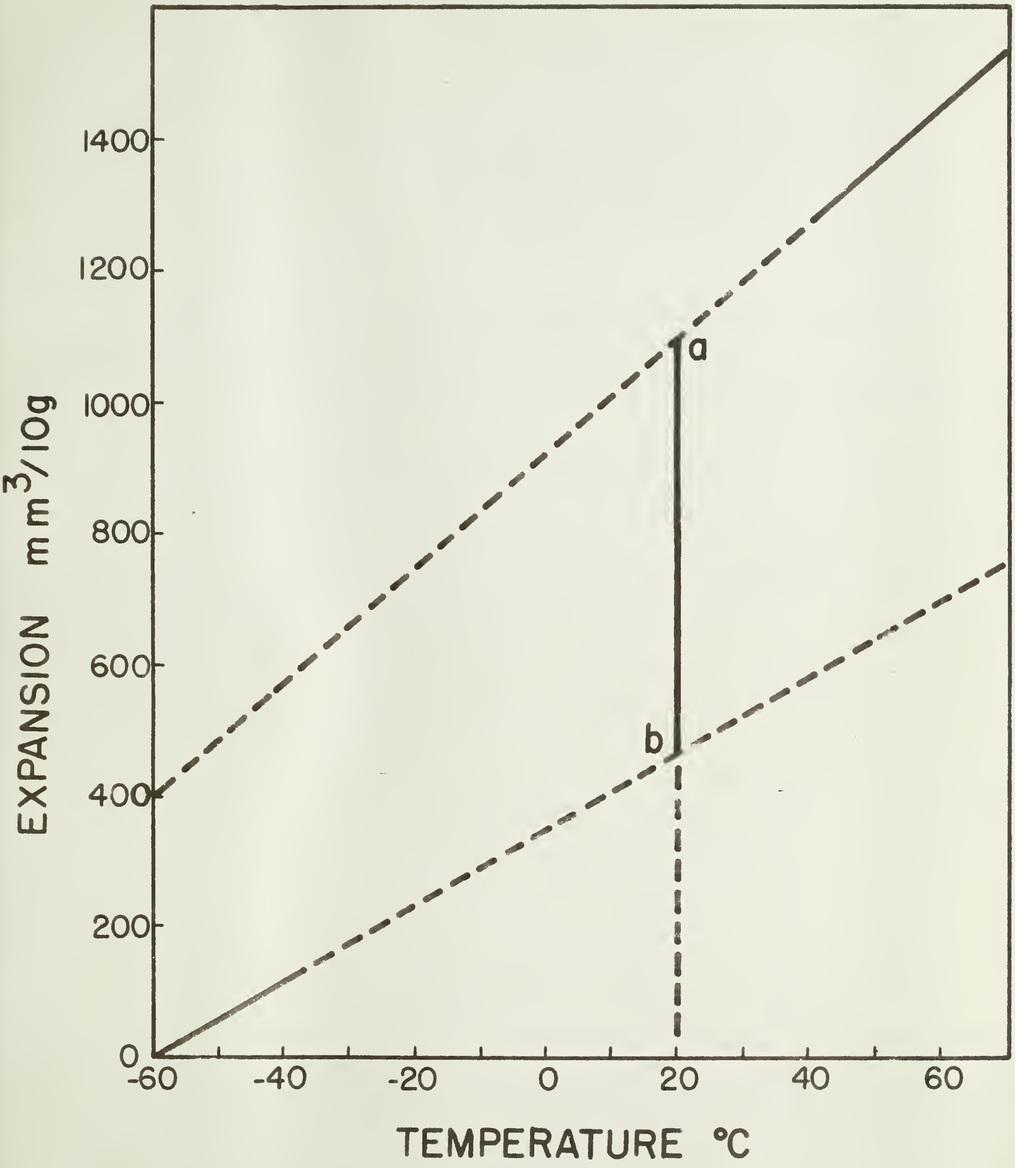


Figure 3. Thermal expansions of solid and liquid butterfat (extrapolated), and melting dilation at 20°C. (distance ab).

Table 3.

Melting dilations of butterfat at different temperatures

Temperature °C.	Melting dilation $mm^3/10$ g
10	624
12	629
14	635
16	640
18	646
20	651
22	656
24	662
26	667
28	673
30	678

The percentage of solid fat in a sample at any one temperature equals the experimentally found melting expansion at that temperature (D_t) divided by the melting dilation at t°C., multiplied by 100.

The technique followed was a dynamic one, i.e., the temperature of the bath containing the dilatometers was increased gradually without interruption at the measuring temperatures. The rate of temperature increase of the bath was 10°C. per hour. No complete equilibrium was thus obtained at any one temperature and, therefore, all values reported are to be considered as comparative rather than absolute. However, with this low rate of temperature increase the values obtained should not differ greatly from the true solid fat contents.

Calorimetry. For the measurement of the total heat content of butter and butterfat between 15° and 55°C. a calorimeter of the type described by Søltoft (99) was used. The calorimeter consisted of a Dewar flask surrounded by a well-insulated heating coil which could be regulated to keep the contents of the Dewar flask at constant temperature. In the Dewar flask was fitted a metal can, filled with mineral oil and provided with a small heater, a stirrer and a Beckman thermometer.

Twenty-gram samples of butter or butterfat contained in small thin-walled aluminum cans were introduced into the oil bath and the resulting temperature drop registered. The temperature drop represents the heat of fusion of the crystalline fat plus the specific heat of the sample over the observed temperature range. The apparatus was standardized by measuring the temperature drop with the cans containing water only. A temperature drop of 1°C. was found to be equivalent to a loss of 227 calories.

RESULTS

Microscopy. Observations under polarized light revealed the crystal structure of the continuously made butter to be characteristic and widely different from that of conventional butter. In the latter butter type the crystalline fat is present largely in globular form and the peripheral birefringent layer of each globule appears as a luminous tetrad. In the continuously made butter, on the other hand, there was never any evidence of the presence of globular fat, and the crystals may be of relatively large size and of irregular form. There was a definite indication of a greater crystalline fat content in winter butter, and this was equally true for both butter types (figs.4, 5, 6 and 7).

The moisture distribution was found to be much finer in continuously made than in conventional butter. Typical results taken from a large number of measurements are presented in table 4. It is readily seen that the preponderance (70%) of moisture droplet volume was within the 0-3 micron range in continuously made butter, whereas this size range comprised only one third of the droplet volume in conventional butter. Figures 8 and 9 are photomicrographs of moisture

Fig. 4. Polarized light photomicrograph of the crystal structure in conventional summer butter.

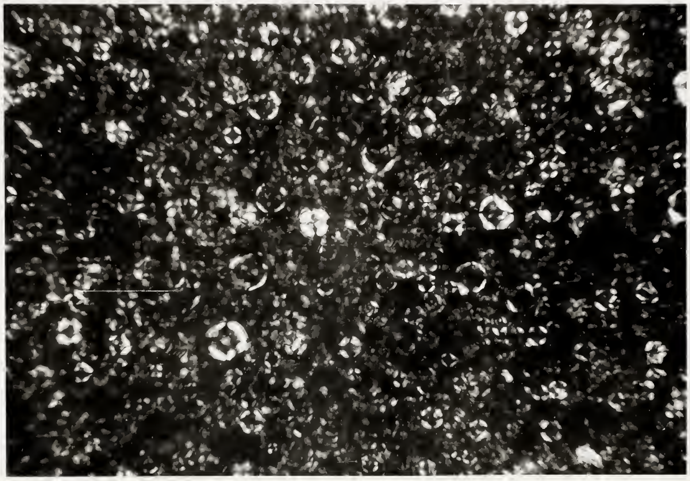


Fig. 5. Polarized light photomicrograph of the crystal structure in conventional winter butter.

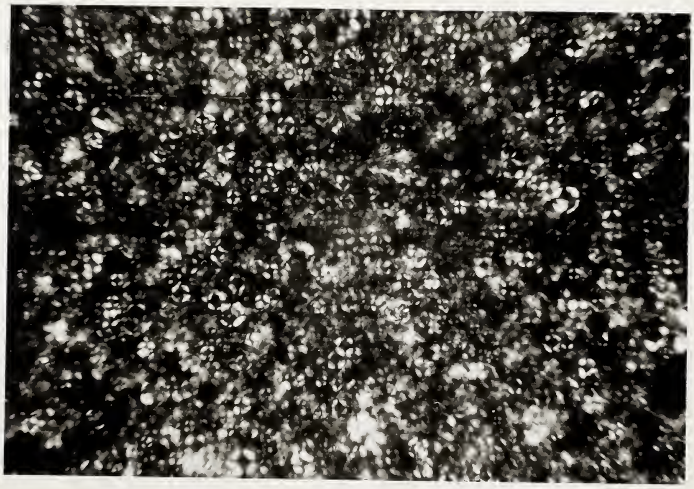


Fig. 6. Polarized light photomicrograph of the crystal structure in continuously made summer butter.

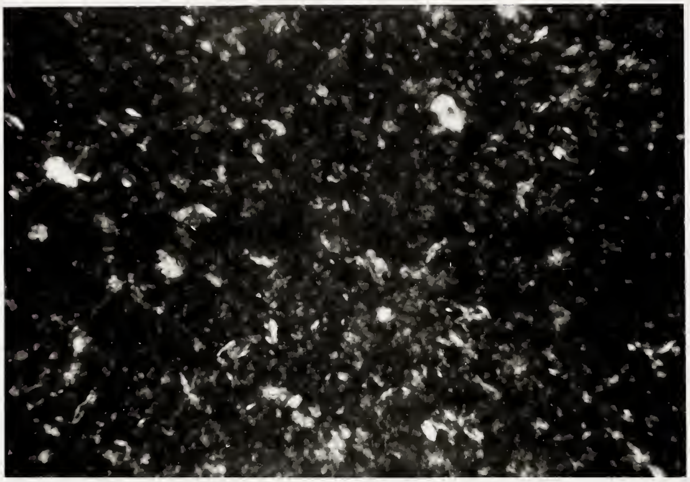


Fig. 7. Polarized light photomicrograph of the crystal structure in continuously made winter butter.

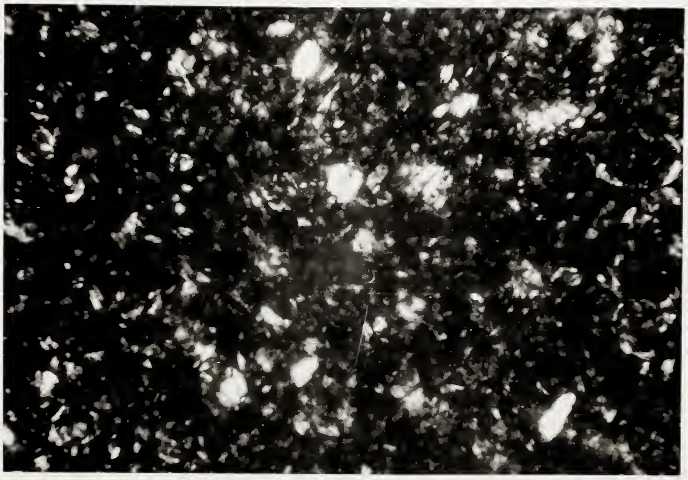


Table 4. Moisture distribution in conventional and continuously made butter

Percent of total moisture volume taken up by different globule size ranges.

Butter type	Diameter of droplets in microns				
	0-3	3-5	5-10	10-15	15-25
Conventional	33.4	19.3	23.5	20.0	3.8
Continuous	69.8	14.9	12.0	3.3	-

Fig. 8. Photomicrograph of the moisture distribution in conventional butter (magnification 750 x).

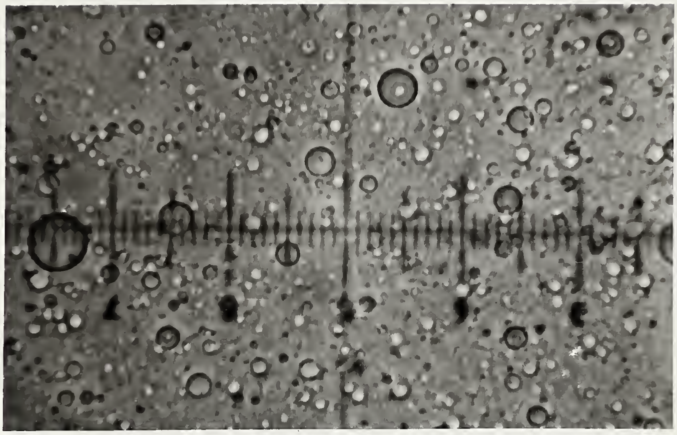
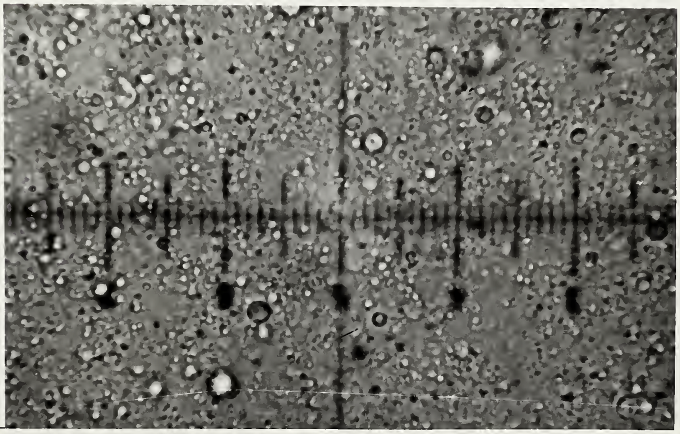


Fig. 9. Photomicrograph of the moisture distribution in continuously made butter (magnification 750 x).



distribution in representative samples of the two butter types.

Hardness. For a period of one year, butter samples were collected weekly from two local creameries. One manufactured butter by the continuous method, the other by the conventional method. Fig. 10 gives the monthly averages of hardness of each butter type as measured by the penetrometer method and fig. 11 as measured by the sectility method. The penetrometer and sectility values show a high correlation (for conventional butter, $r = 0.98$, and for continuously made butter, $r = 0.95$, both significant at the 1% level). It is to be noted that the butter types follow the same general hardness trend throughout the year (for penetrometer values $r = 0.81$, significant at the 1% level). This indicates that the difference in physical structure is responsible for the greater hardness of the continuously made butter, as it was established previously (113) that the chemical composition and some physical properties of the butterfat of these two Edmonton creameries do not differ significantly. The maximum hardness of both butters occurred in November-December, when the softening point of the butterfat in this region is at maximum value; and, conversely, minimum butter hardness and minimum

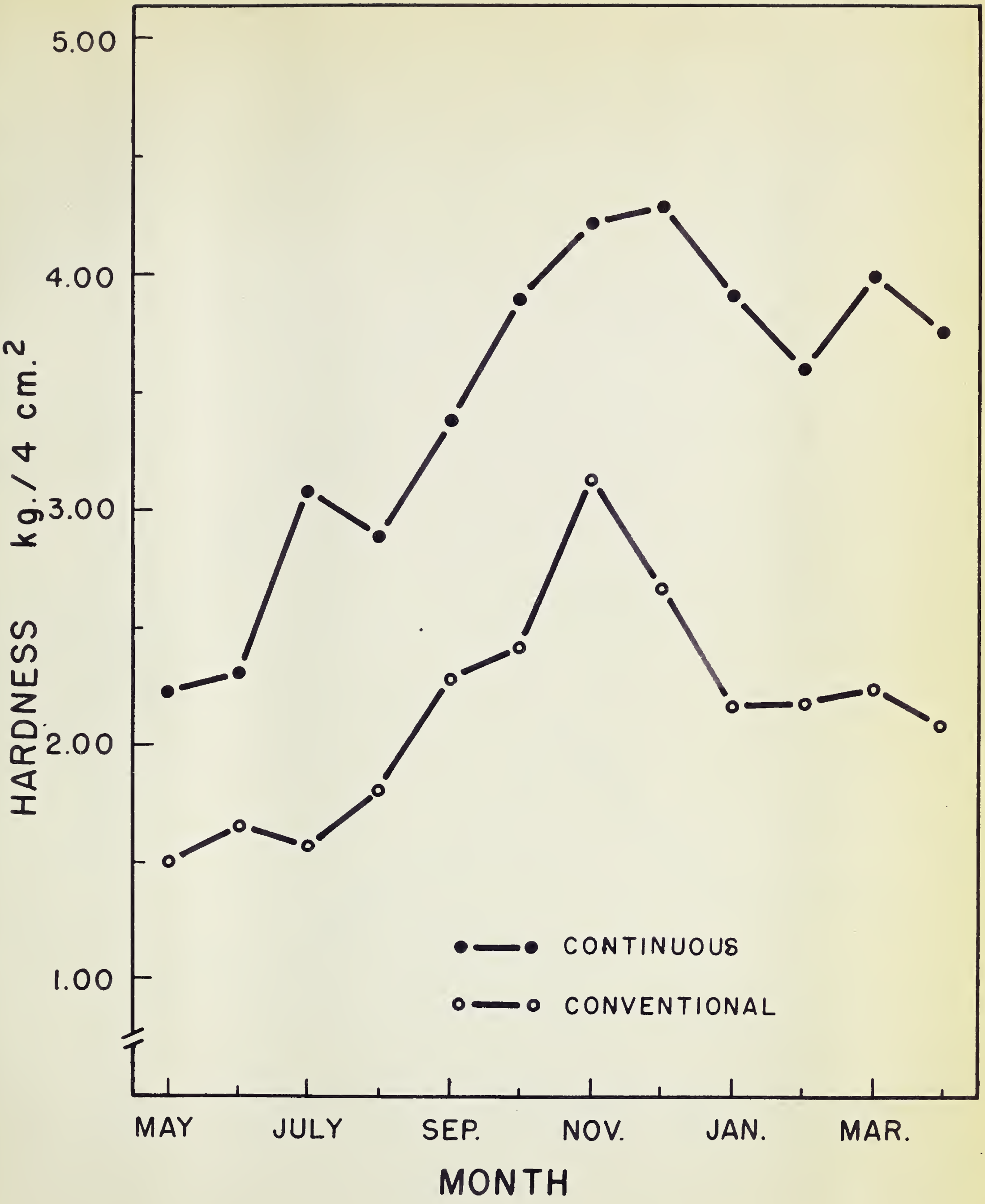


Figure 10. Seasonal variation in hardness of conventional and continuously made butters as measured by the penetrometer method.

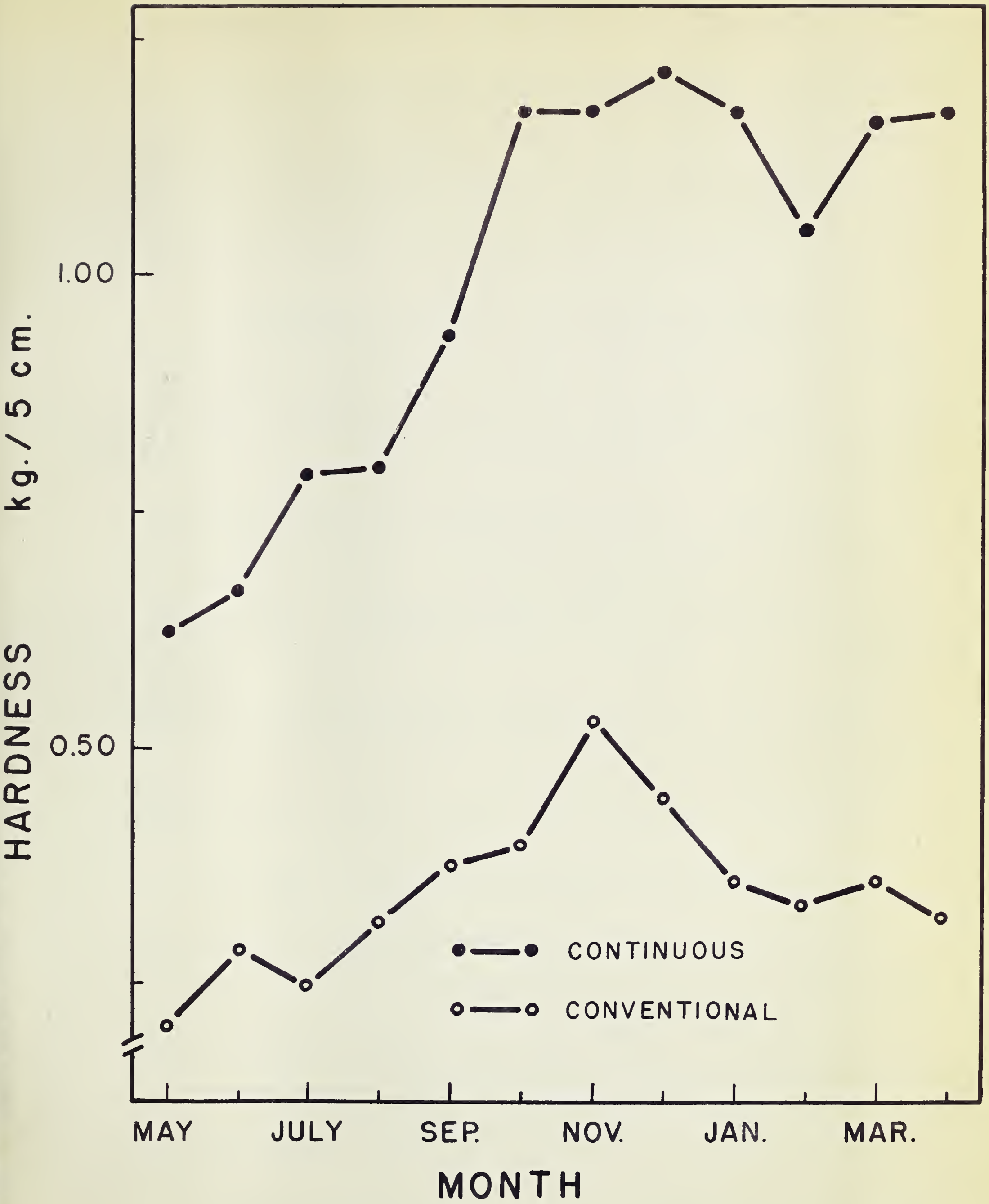


Figure 11. Seasonal variation in hardness of conventional and continuously made butters as measured by the sectility method.

softening point of the butterfat coincided seasonally.

It is evident from these figures that on any sampling date the continuously made butter was harder than the conventional butter. The difference was found to be significant at the 1% level.

A remarkable further difference in hardness properties is revealed in these figures. When a point of equal hardness is chosen on the penetrometer curves of each butter type, it is found that the corresponding sectility values are widely different. The equal penetrometer values of continuously made June and conventional September butter can be taken as an example. The sectility values of these same butters show a wide divergence, indicating that the change in hardness obtained by the use of varying measurement temperatures is different for each type of butter.

Storage of both conventional and continuously made butters at high temperatures had a remarkable softening effect. The effect of storage of 20-22.5°C. was a permanent one, i.e. the butters softened at the high temperatures did not regain their initial hardness by subsequent storage at 5°C.

A typical example of such an experiment is given

in table 5. The butter's were held for one week at $5^{\circ}C.$, followed by two weeks at $22.5^{\circ}C.$ and finally for two weeks at $5^{\circ}C.$ Polarized light microscopy of the butters stored at this high temperature indicated a definite reduction in crystalline fat content (figs. 12, 13, 14, and 15). The reduced hardness is thus most likely the result of a reduction in the quantity of crystalline fat.

Oiling-off. Weekly samples of conventional and continuously made butter taken over the period of one year were tested for oiling-off properties. The results of the oiling-off measurements are presented in fig. 16 as monthly averages. Although there is a marked similarity in the curves for the two types of butter, the differences between the two butter types were found to be highly significant. As it may be assumed that the composition of the fat in corresponding samples of the two butter types did not differ significantly (113), the differing oiling-off properties indicate a dissimilarity in physical structure.

Maximum and minimum oiling-off values occurred in June and October-November, respectively, and the difference between high and low values is approximately 7% for each butter type. Values for continuously made

Table 5. Influence of storage at 22.5°C. on butter hardness

Butter type	Penetrometer hardness (Kg/4cm^2), after				
	1 wk.	2 wks.	3 wks.	4 wks.	5 wks.
continuous	2.76	1.20	1.25	1.18	1.20
conventional	1.88	1.16	1.18	1.14	1.16

(One week at 5°C., followed by 2 weeks at 22.5°C., then two weeks at 5°C.)

Fig. 12. Polarized light photomicrograph of conventional butter before storage at 22.5°C.

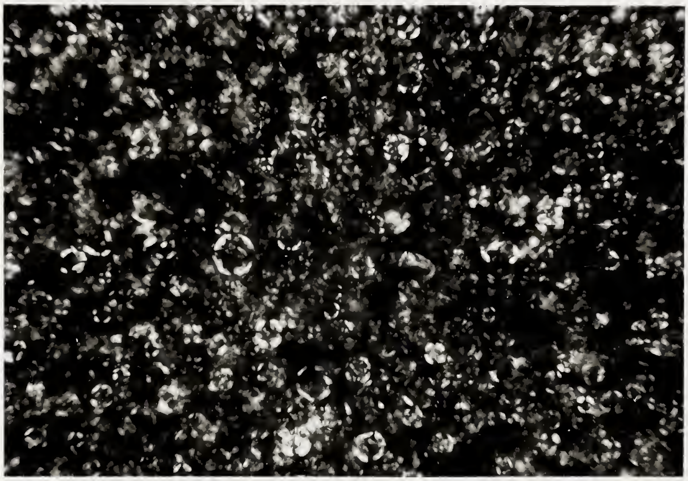


Fig. 13. Polarized light photomicrograph of conventional butter after storage at 22.5°C.

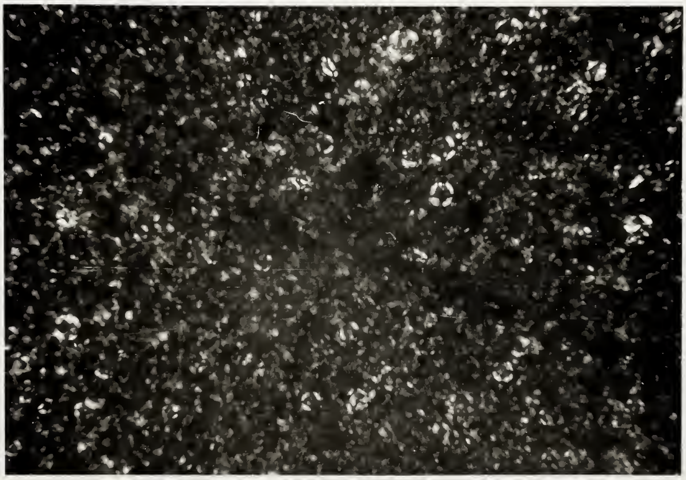


Fig. 14. Polarized light photomicrograph of continuously made butter before storage at 22.5°C.

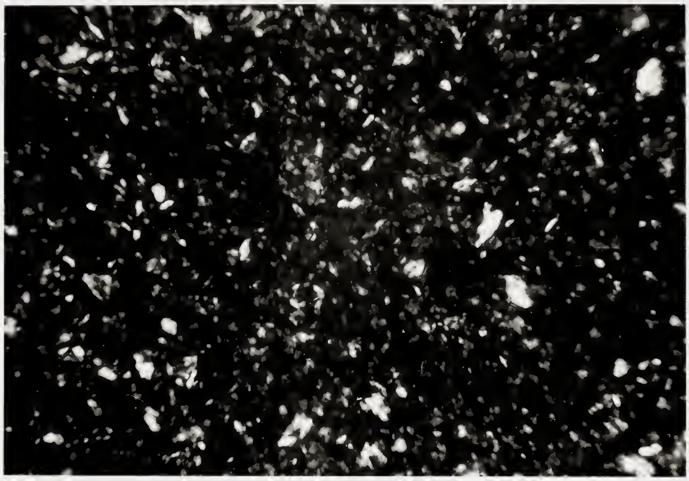
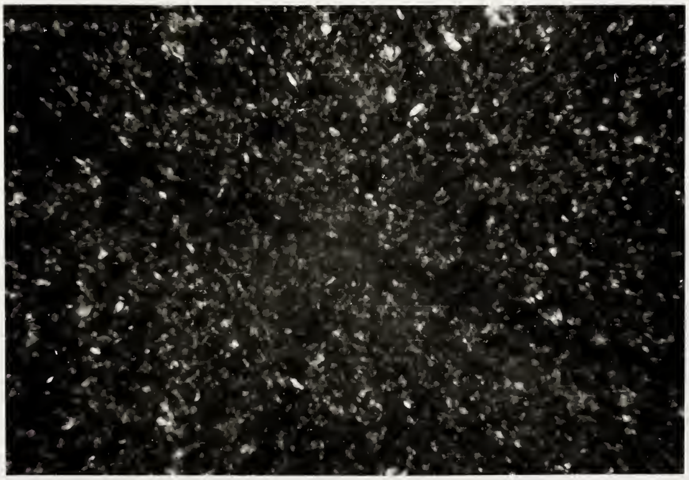


Fig. 15. Polarized light photomicrograph of continuously made butter after storage at 22.5°C.



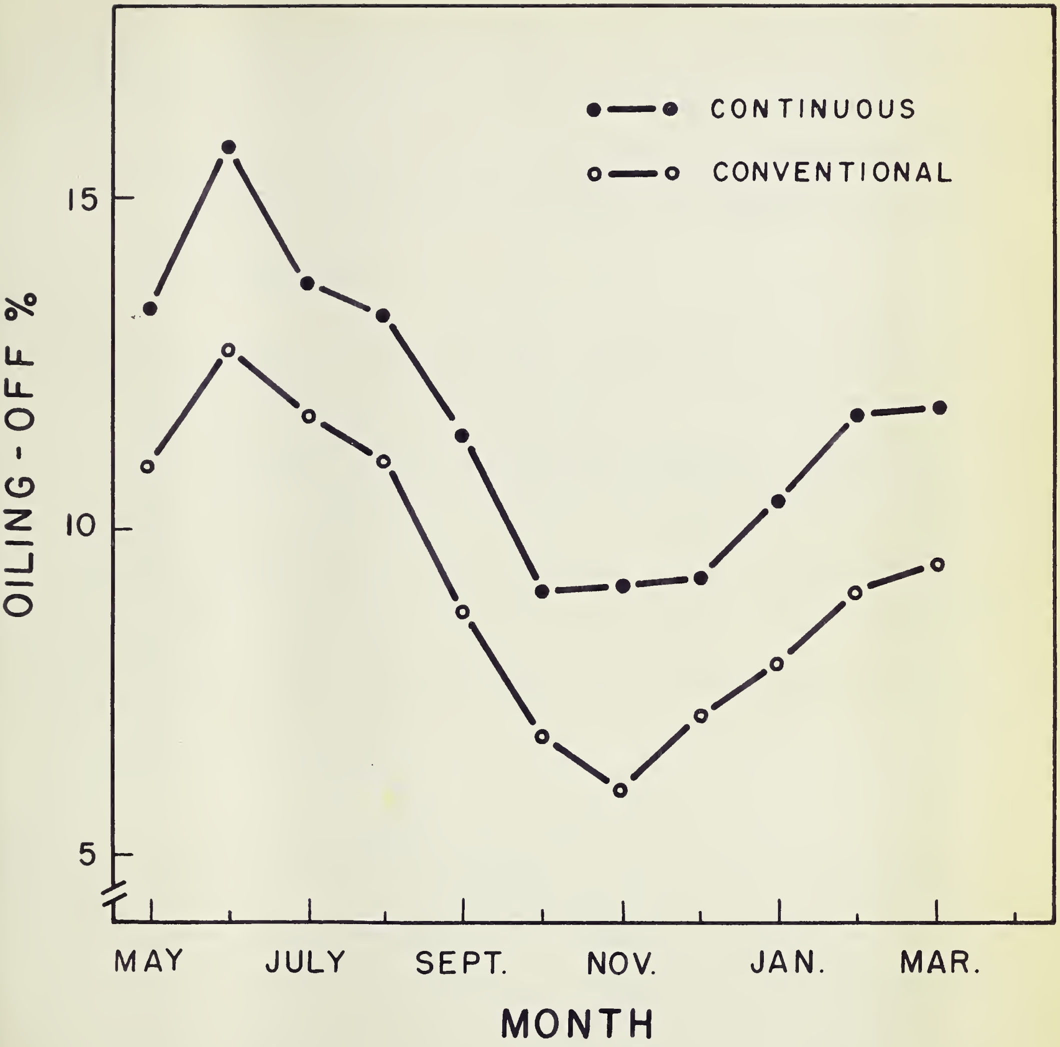


Fig. 16. Seasonal variation in oiling-off properties of conventional and continuously made butters.

butter ranged from 9.1 to 15.9% and for conventional butter from 6.1 to 12.8%. Seasonal variations were considerable and of greater magnitude than differences between the butter types at any one time. Seasonal variability closely followed seasonal variations in chemical composition of the butterfat. The June oiling-off maxima and October-November minima occurred simultaneously with the minimum and maximum hardness of the butters.

Gas content. While it was claimed that nitrogen gas was added to the butter previous to the cooling and working stage in the commercial creamery using the continuous method, the butter was nevertheless found to be practically free of gas. A large number of determinations gave values ranging from 0 to 0.2%, but occasionally a sample with a gas content up to 0.4% was encountered.

The gas content of conventional butter produced in this region was determined for printed and non-printed butters of different seasons. As could be expected the density of butter is mainly dependent on gas content. The correlation between gas content and density was high (r = 0.94 significant at 1% level). The average gas content of winter and summer butters was 3.4 and 4.0% respectively (t = 4.03, D.F. = 80,

significant at 1% level). Printing of butter, after storage, resulted in a remarkable lowering of the gas content (table 6). The average gas content before printing was 3.8% and after printing 1.95% ($t = 10.2$, D.F. = 21, significant at 1% level).

Variations in the disperse phase. To determine the influence of variations in gas content on the hardness of continuously made butter varying amounts of nitrogen were incorporated into butters made in the experimental continuous buttermaking machine. Increased gas content was found to result in a highly significant hardness reduction (table 7). The regression coefficient of hardness on gas content was $b = -0.18$ Kg/4 cm^2.

The following experiments were conducted to determine the influence of the presence of globular fat on butter hardness. Samples of conventional butter and the cream that was used for their manufacture were obtained from a commercial creamery. The creams were reseparated to contain over 80% fat, standardized to 16% moisture and salt was added. Butters were then made in the experimental continuous buttermaking machine from the melted butters, from the plastic creams, and from equal parts of melted butter and plastic cream. In this way there were obtained conventional butter, and

Table 6. Density and gas content of conventional butters before and after printing

Non-printed		Printed	
Density	Gas %	Density	Gas %
0.914	4.5	0.940	1.5
0.921	3.3	0.939	1.9
0.927	2.8	0.937	1.7
0.927	3.0	0.942	1.8
0.916	3.7	0.947	1.5
0.923	3.2	0.942	1.9
0.934	2.9	0.939	1.9
0.928	3.2	0.948	1.5
0.922	3.3	0.944	1.4
0.909	5.1	0.939	1.4
0.917	3.8	0.934	2.1
0.918	4.1	0.944	1.4
0.917	4.2	0.931	2.6
0.907	5.7	0.931	2.6
0.914	4.9	0.931	2.2
0.924	4.0	0.929	2.4
0.925	2.8	0.933	2.2
0.933	2.6	0.935	2.1
0.923	3.6	0.941	1.6
0.917	4.5	0.947	1.1
0.908	5.0	0.921	3.2
0.919	4.3	0.927	2.8
Ave.0.921	3.84	0.937	1.95

Table 7. Influence of gas content on the hardness of continuous type butter

Butter No.	Gas %	Hardness Kg/4 cm^2
1	0	2.60
	1.4	2.38
	2.0	2.32
	3.3	2.00
2	0	2.88
	1.3	2.44
	7.5	1.68
3	0	2.90
	0.8	2.78
	1.4	2.36
4	0	3.54
	4.0	2.88
5	0	3.20
	1.8	2.92
	3.9	2.44
	5.2	2.10

continuously made butters with varying globular fat content, all of which had the same chemical composition. Hardness values of the butters obtained in a number of these experiments are listed in table 8. Hardness of the butters made from the molten ingredients, plastic cream, or a mixture of these were identical, indicating that the presence of globular fat under these conditions had no effect on hardness. The conventional butters, nevertheless, were much softer than the butters made from the same ingredients in the experimental continuous buttermaking machine indicating that the speed of cooling and as a result the condition of the fat phase are of major importance in determining butter hardness.

Setting. A quantity of continuously made butter was taken from the discharge end of the texturator and kept at constant temperature, 5°C., in a waterbath. Hardness was measured at this temperature by the sectility method, hourly for 6 hours, and daily thereafter for 7 days. Conventional butter taken from the churn at 12.5°C. was kept at this temperature and hardness measured at 12.5°C. by the penetrometer method. Results obtained in this manner are presented in figs. 17 and 18. Sectility hardness of the continuously made butter increased

Table 8. Influence of the presence of globular fat on the hardness of continuous type butter

Experiment No.	Hardness ($kg/4\ cm^2$)			
	Conventional butter	Continuously made from melted butter	Continuously made from half melted butter half plastic cream	Continuously made from plastic cream
1	1.40	2.40	2.40	2.40
2	1.20	1.80	1.84	1.76
3	1.80	2.72	2.78	2.74
4	1.92	2.78	2.84	2.72
5	1.76	2.56	2.64	2.48
6	1.48	2.18	2.26	2.26

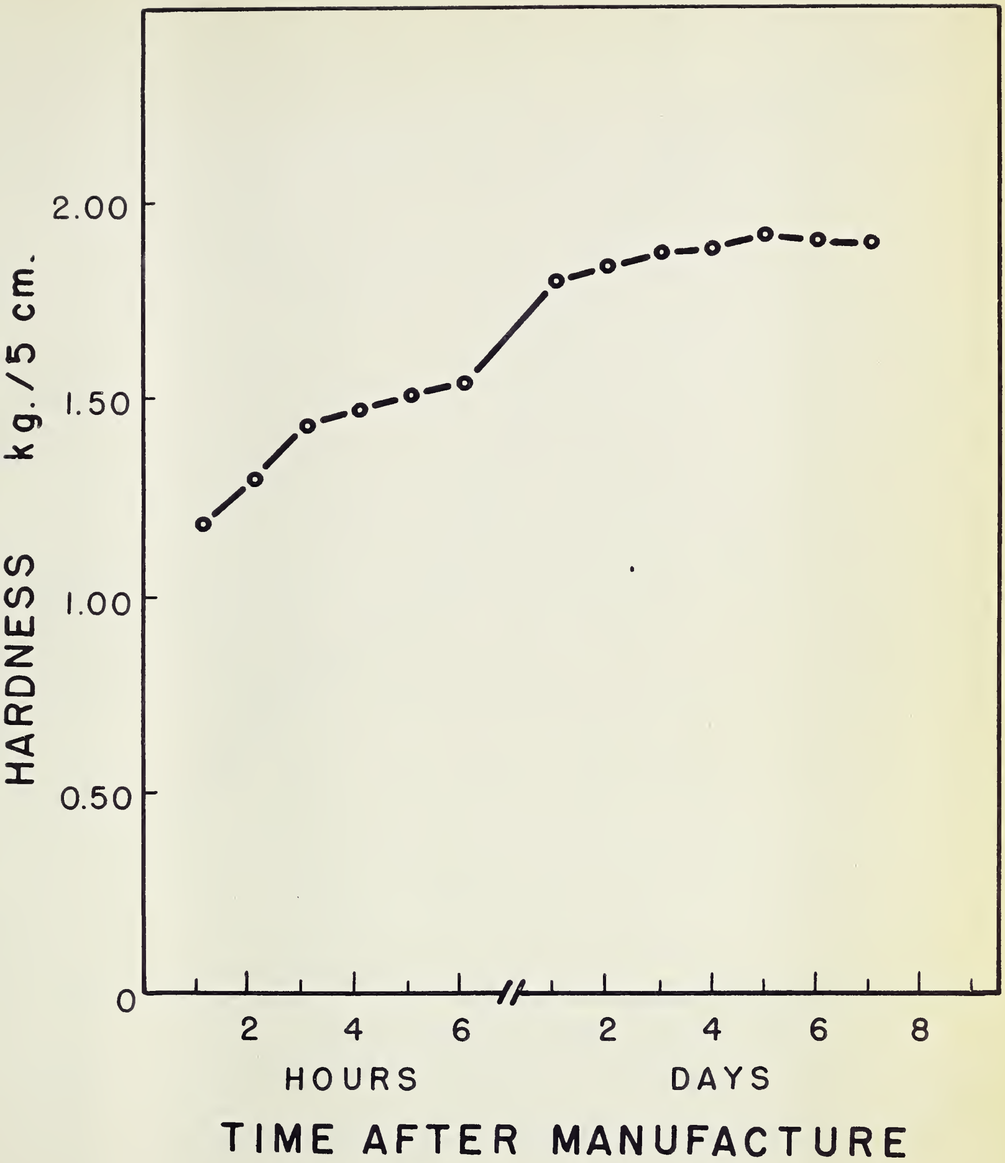


Fig. 17. Sectility hardness of continuously made butter stored at 5°C. after manufacture.

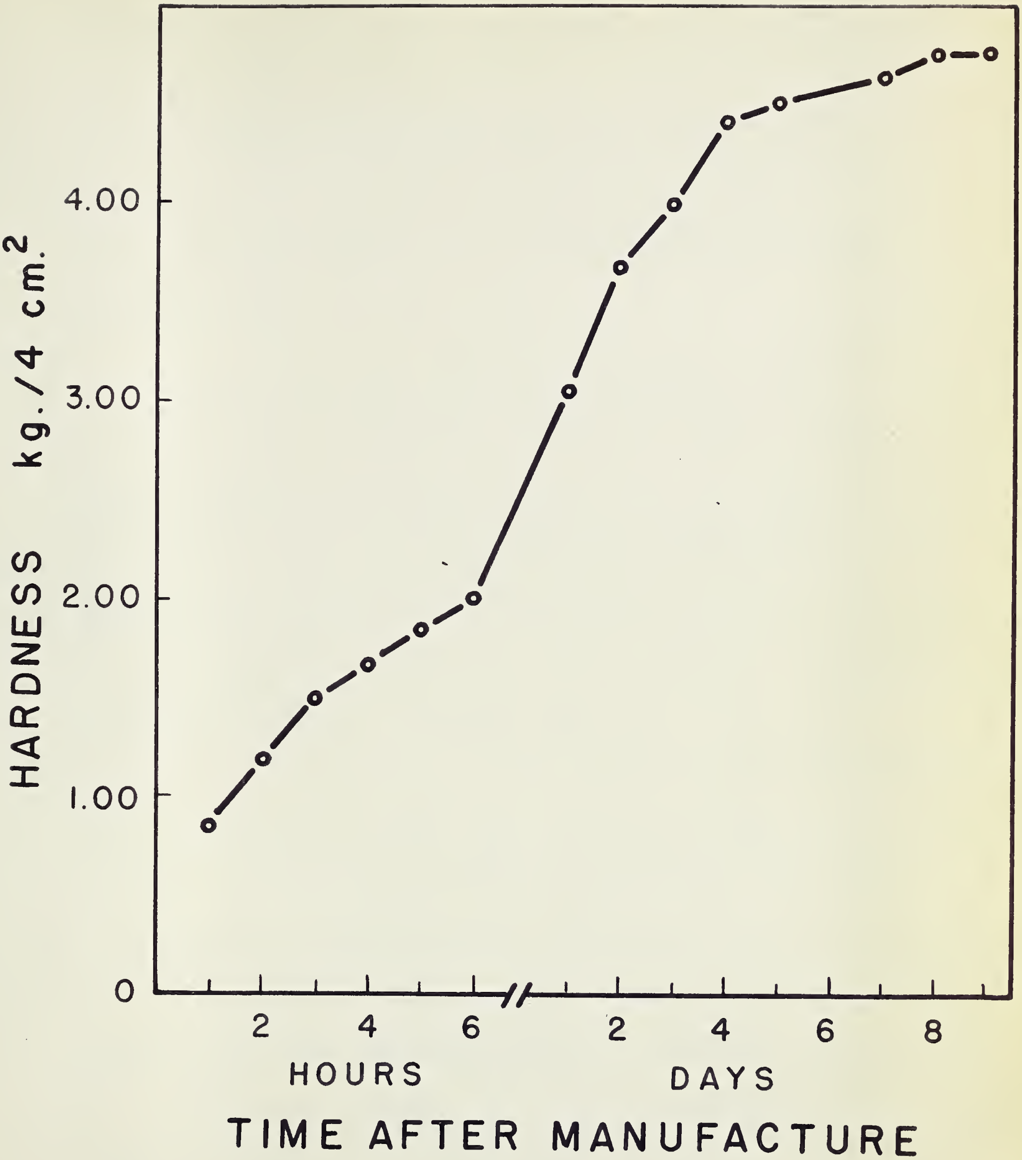


Fig. 18. Penetrometer hardness of conventional butter stored at 12.5°C. after manufacture.

rapidly for the first 6 hours and less rapidly thereafter. The conventional butter also showed a remarkable hardness increase under these conditions. As in this way the influence of temperature changes during storage is eliminated, these experiments indicated that considerable hardness changes take place in both butter types independent of storage temperatures.

Butters of both types with varying initial hardness were obtained at different times of the year, stored at a storage temperature of approximately 5^{o}C. and hardness measured by the penetrometer method. Results are presented in figs. 19 and 20 for June and December butters, which are representative of seasonal hardness extremes. Curves A are for setting of conventional and curves B for continuously made butter. In all cases the major part of setting took place during the first week after manufacture. In soft conventional summer butter setting continued to the end of the first month but in conventional winter butter setting was not complete after two months. At the end of two months' storage the hardness increases were as listed in table 9. The relative hardness increases of conventional butter were considerably higher than those

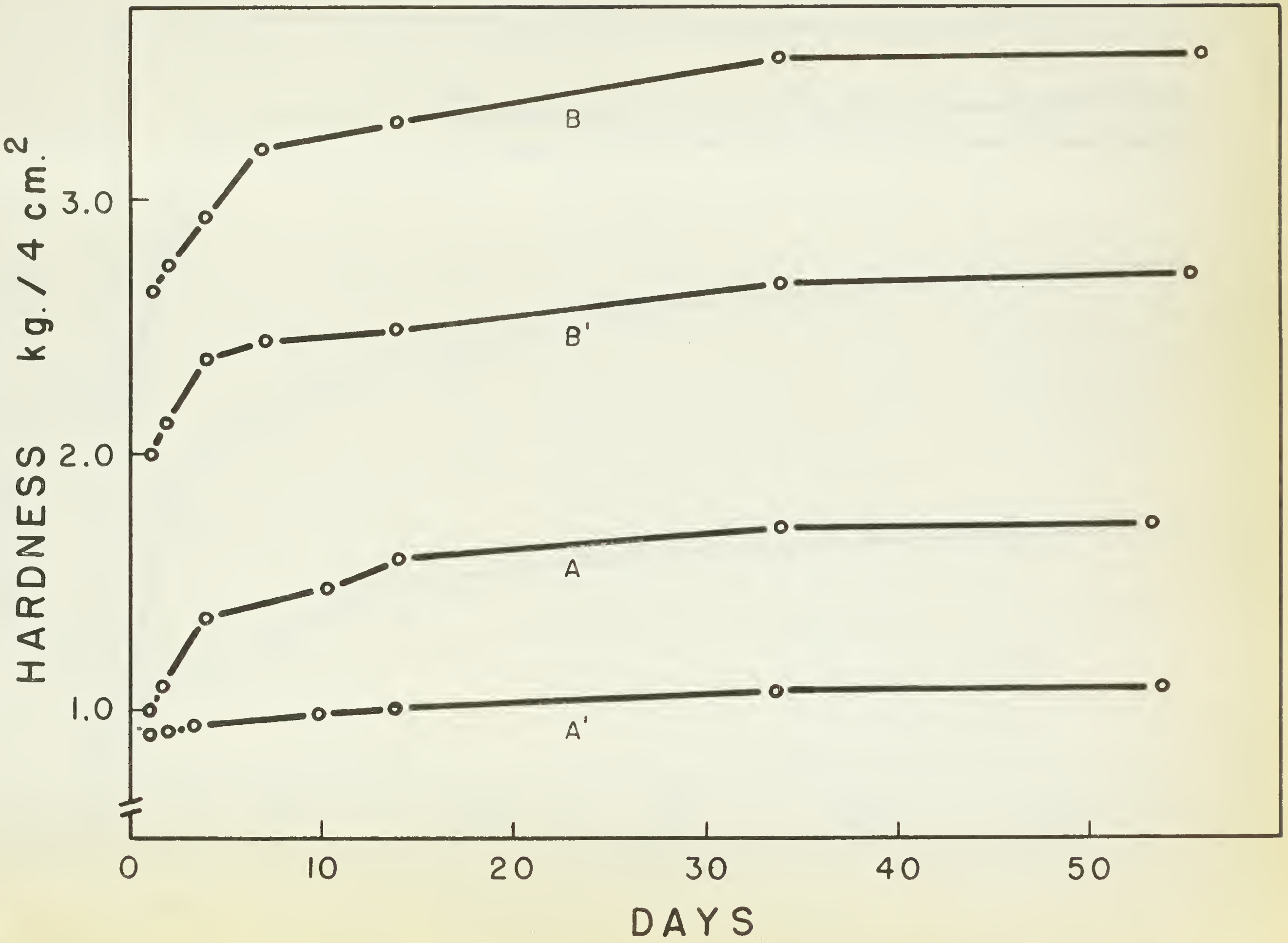


Fig. 19. Setting of conventional (curves A) and continuously made (curves B) summer butters before and after printing

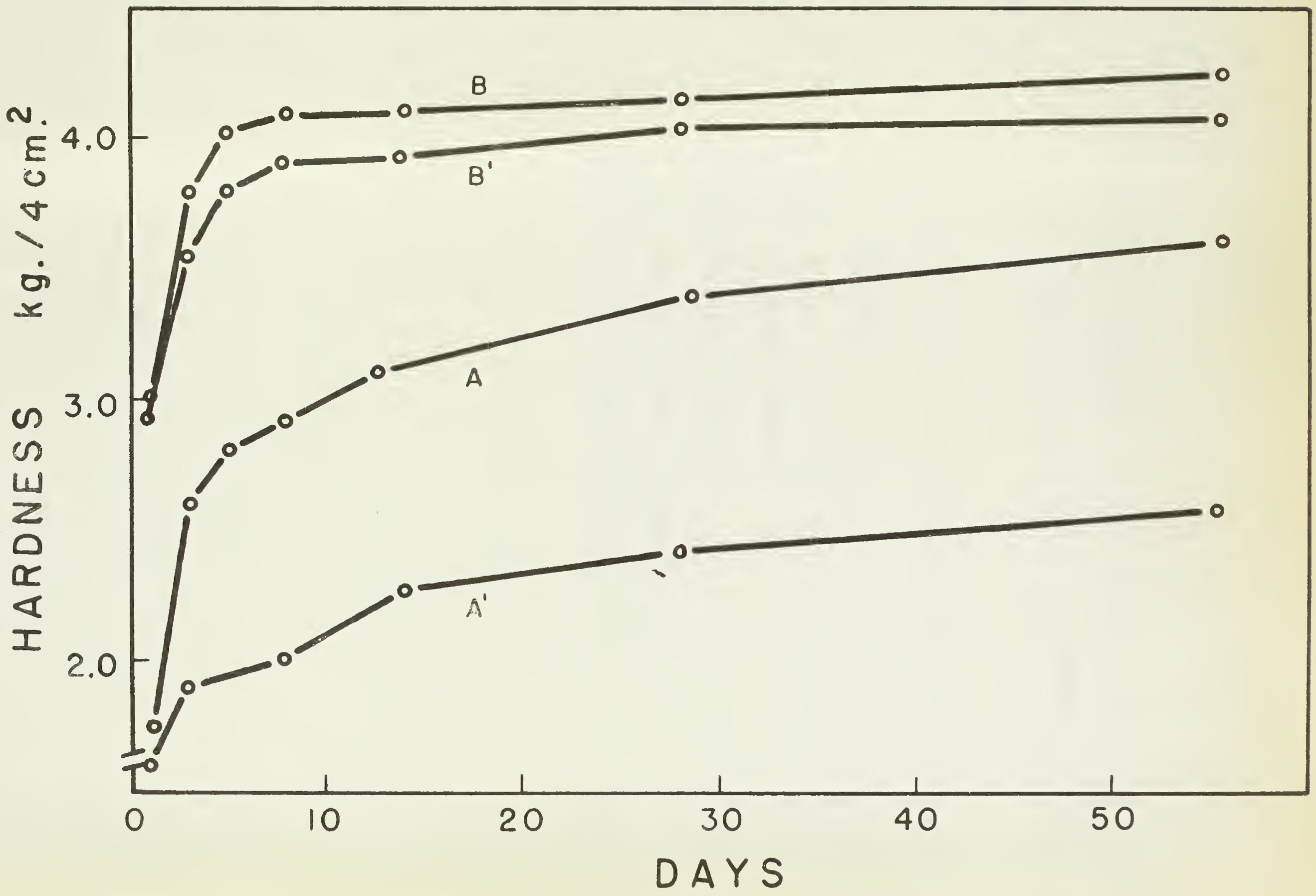


Fig. 20. Setting of conventional (curves A) and continuously made (curves B) winter butters before and after printing

Table 9. Relative penetrometer hardness increases of butters after two months' storage

Butter	Hardness increase %
Conventional, summer	75
Conventional, winter	106
Continuously made, summer	35
Continuously made, winter	42

of continuously made butter, both in summer and winter samples.

Setting was also measured on the butters described above after they had been put through a commercial printing machine (curves A' and B' in figs. 19 and 20). This gives the butter an additional working treatment which tends to break down any crystal structure which might have been present. The conventional butter was printed after being held at 5°C. for 1 or 2 days while the continuously made butter was printed immediately after leaving the texturator at approximately 5-7°C. Printing resulted in a lowering of the initial hardness and a striking reduction in the extent of setting in all except the continuous winter butter. This hard butter showed little reduction of the extent of setting after printing. The soft conventional summer butter displayed only a very limited setting after printing.

To compare setting of butter made from the same fat but with different cooling treatment of cream, conventional butters were made from cream cooled in a relatively slow way and from the same cream cooled quickly. The butter made from the rapidly cooled cream was harder initially than that made from the slowly

cooled cream and the difference increased as setting progressed, i.e. the extent of setting of the former butter was greater (fig. 21). Polarized light microscopy of these butters showed that the butter prepared from rapidly cooled cream had a higher content of crystalline fat than the butter made from the slowly cooled cream (figs. 22 and 23).

The influence of variations in storage temperature on setting is illustrated in fig. 24 which represents the hardness values of conventional butter when stored at either 5°C. or 15°C. It was found that the hardness increase was always greater at 5°C. than at 15°C. The influence of low temperature (-20°C.) storage on setting is given in fig. 25. The setting of conventional butter stored at 5°C. immediately after manufacture is represented by curve A. Some of the same butter was placed at -20°C. immediately after manufacture, kept at that temperature for three weeks, and then removed to 5°C. storage. From this moment on the hardness increased in the same way (curve B) as that of the butter that was directly placed at 5°C. When the butter was first allowed to set at 5°C. for three weeks, then stored at -20°C. for three weeks and subsequently removed to 5°C. (curve C) the setting was resumed

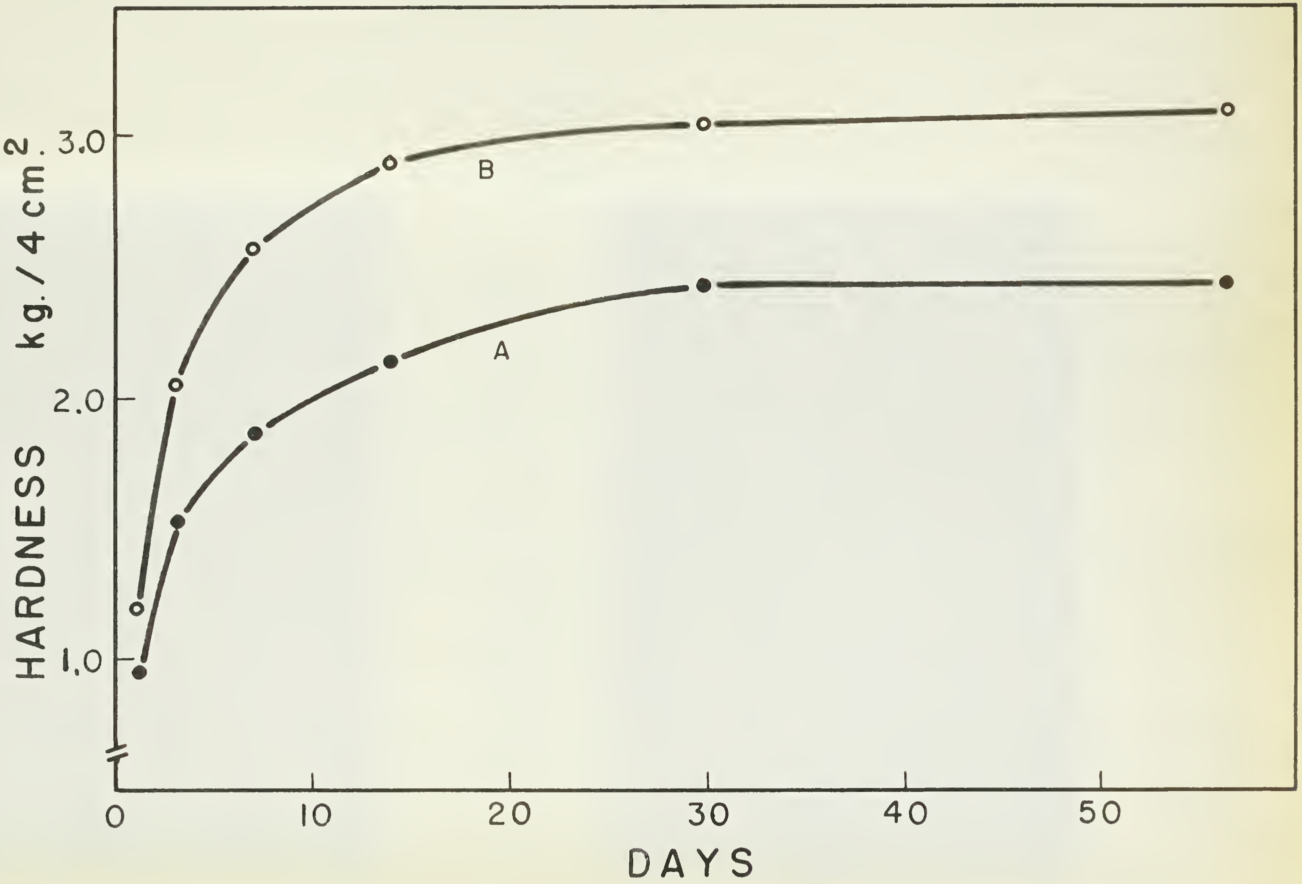


Fig. 21. Setting of butters made from the same cream cooled either slowly (curve A) or quickly (curve B)

Fig. 22. Polarized light photomicrograph of conventional butter prepared from rapidly cooled cream.

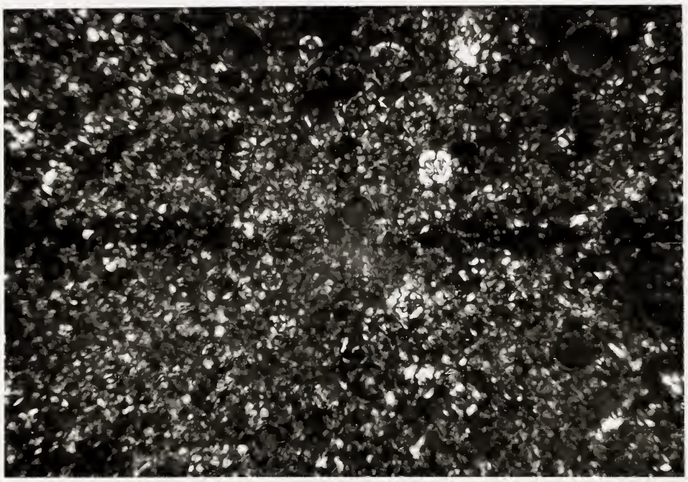
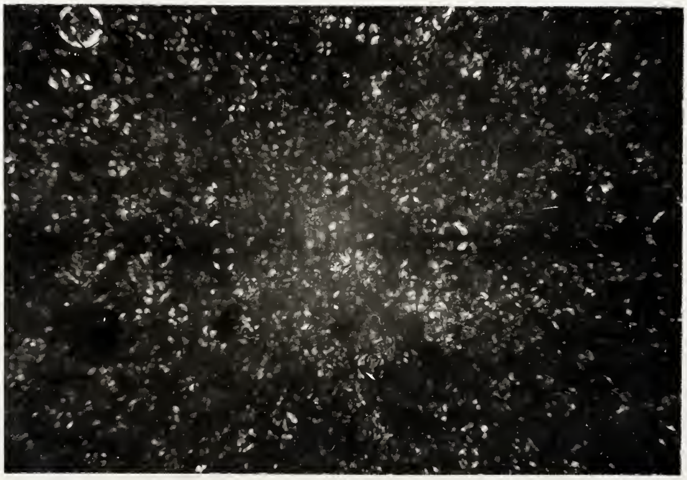


Fig. 23. Polarized light photomicrograph of conventional butter prepared from slowly cooled cream.



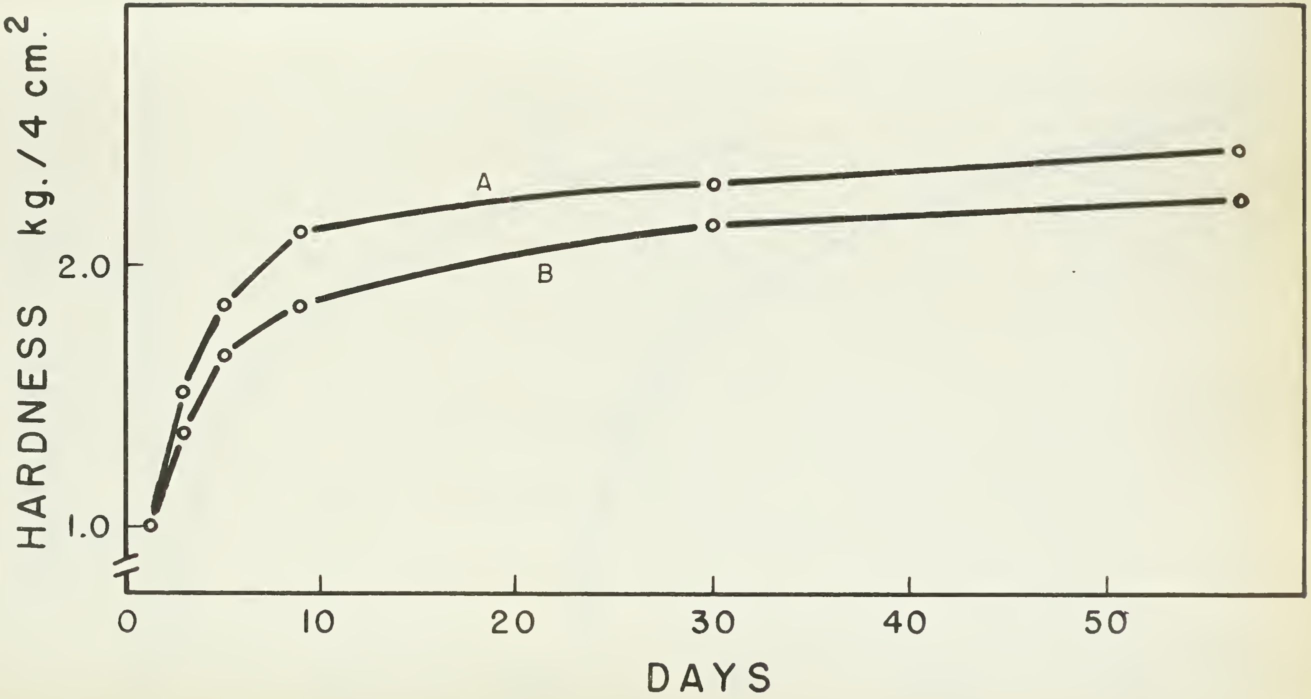


Fig. 24. Setting of conventional butter when stored either at 5°C. (curve A) or at 15°C. (curve B)

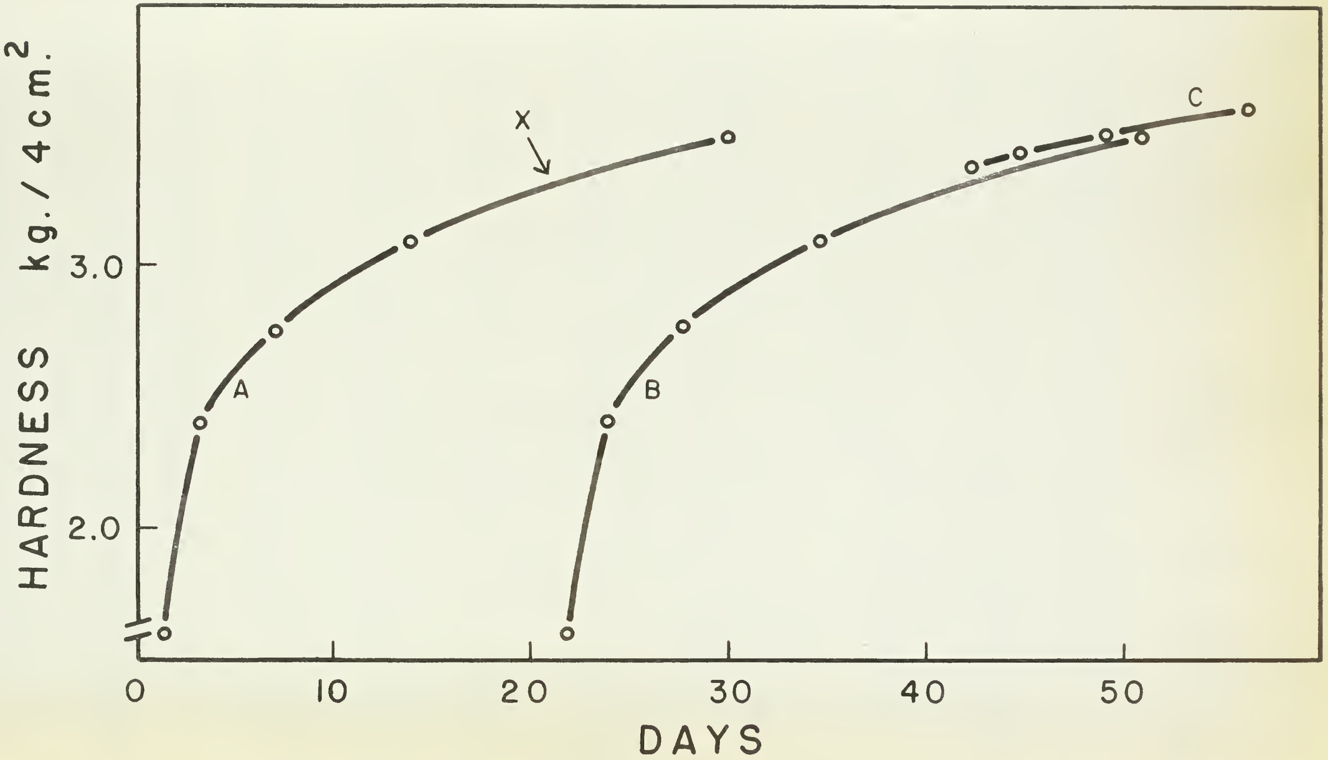


Fig. 25. Influence of low temperature storage on setting. Butter stored at 5°C.(curve A)immediately after manufacture. Same butter stored at -20°C. for 3 weeks, followed by storage at 5°C. (curve B). Same butter stored at 5°C. for 3 weeks, followed by storage at -20°C. for 3 weeks, subsequently stored at 5°C. (curve C).

exactly at the point at which it was interrupted by freezing. This experiment indicates that freezing stops the setting process but that on increasing the temperature to that of normal storage conditions setting is resumed without being fundamentally changed. The observed phenomena are identical with those exhibited by continuously made butter. The results of a typical experiment with continuously made butter are given in table 10.

Butterfat crystallization. As a general rule small crystal particles will be obtained when a rapid temperature drop and/or violent agitation are applied during crystallization. On the other hand, with slowly decreasing temperatures and quiescent conditions, formation of large crystals is favored. Butterfat is no exception to this rule as is evident from figs. 26 and 27. Relatively rapidly cooled fat yields crystals of a size below 1 micron whereas slow cooling results in the formation of crystals up to 100 microns in size.

The occurrence of crystallization in a fat can be detected by measurement of the liberated heat of crystallization. To ascertain whether any crystallization occurs in butter of both types immediately after manufacture the possible occurrence

Table 10. Influence of freezing on hardness of continuously made butter

Storage	Penetrometer hardness ($Kg/4\ cm^2$)
Initial	2.80
1 week at 5°C.	3.72
2 more weeks at -20°C.	3.72
2 more weeks at 5°C.	3.86

Fig. 26. Polarized light photomicrograph of rapidly cooled butterfat.

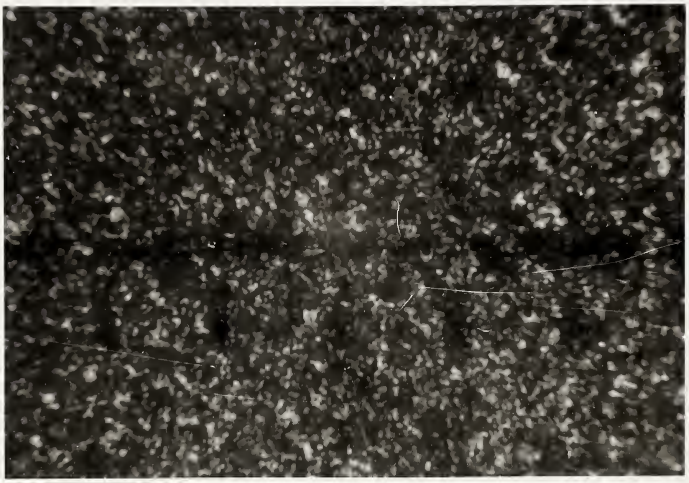
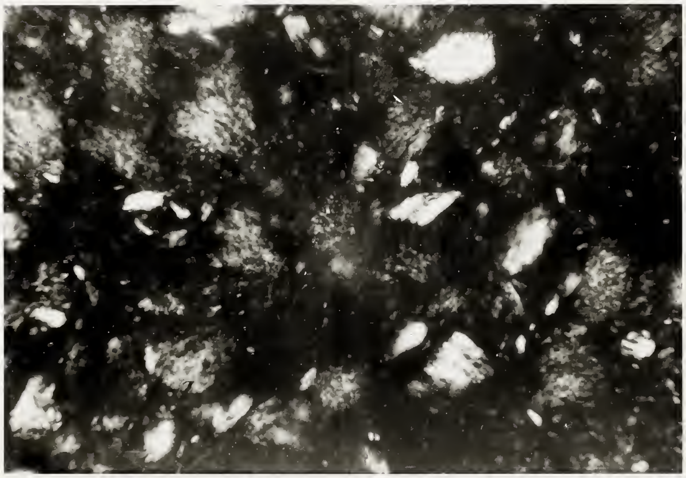


Fig. 27. Polarized light photomicrograph of slowly cooled butterfat.



of a temperature rise was investigated. A large Dewar flask was tempered to the prevailing butter temperature and filled with butter taken from the churn or from the texturator. An example of temperature readings obtained in this way is recorded in table 11. While there was no temperature rise in conventional butter, a considerable increase (usually 3-5°C.) took place in the continuously made butter. The temperature rise of continuously made butter is not restricted to the time after discharge from the texturator. In the texturator there is also an increase, usually from 3-5°C. The total increase in temperature from a point immediately after leaving the chiller may thus amount to 6-10°C. It is evident that considerable crystallization takes place during passage of the butter through the texturator and during the first hour after manufacture.

Dilatometry. This technique was used to determine the influence of different cooling rates, the influence of seasonal variations in the chemical composition of butterfat, and the influence of variations in storage temperatures on the ratio of solid to liquid butterfat at different temperatures.

September butterfat only was used for

Table 11. Temperatures of butters stored in Dewar flasks immediately after manufacture

Butter type	Temperature °C.						
	Initial	1/4 hr.	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.
Continuous	8.7	10.5	11.1	11.5	11.8	11.9	11.9
Conventional	14.9	15.0	15.0	15.0	15.0	-	-

measurements of the effect of cooling treatments. The dilatometers containing the fat were warmed to 45°C., and then cooled in either of the following ways: (a) storage of the dilatometers overnight in air at 15°C., (b) immersion in a 15°C. waterbath, (c) immersion in a 10°C. waterbath, (d) immersion in a 5°C. waterbath or (e) immersion in a 0°C. waterbath. The dilatometers were kept in the waterbaths for at least 4 hours to ensure maximum crystallization. The percentages of solid fat found following these treatments are listed in table 12. It is assumed that cooling in waterbaths at decreasing temperatures would affect the subsequent melting behaviour mainly, if not entirely, as a result of higher rates of cooling. The solid fat percentage generally increased with increased cooling rate. There was more solid fat at all measuring temperatures when the dilatometers were cooled in water at 15°C. than when they were cooled in air at the same temperature. The solid fat percentage increased with lower cooling temperatures only within the lower part of the measuring range. Cooling to 5°C. and to 0°C. in water resulted in very little difference in solid fat content. When the increments of expansion were plotted against temperature, differential dilatometric curves (35) were

Table 12. Influence of cooling treatment on the percentage of solid phase in September butterfat

Measurement temperature	Solid fat % when dilatometers cooled in				
	air 15°C.	water 15°C.	water 10°C.	water 5°C.	water 0°C.
(°C.)					
12	-	-	48	56	56
14	-	-	45	52	53
16	29	36	41	47	47
18	27	34	36	40	39
20	24	27	29	32	30
22	19	21	23	24	23
24	16	19	18	19	18
26	13	15	14	15	15
28	10	12	12	12	12
30	7	9	9	9	9

obtained (figs. 28 and 29), they indicate that maximum melting of the rapidly chilled fat was between 18 and 20°C., but of the slowly cooled fat it was between 20 and 22°C.

To determine the influence of seasonal variations June, September and December butterfats were cooled in two ways: (a) immersion of the dilatometers in water at 0°C. or (b) storage of the dilatometers in air at 15°C. The solid fat percentages resulting from this treatment are listed in table 13. With both treatments there was a considerably higher solids content in December fat than in June fat, while September fat gave intermediate values. The differences were especially marked at the higher measuring temperatures, which indicates variations in the content of higher melting glycerides.

It was previously shown that butter held at a temperature of 22.5°C. for 1 week maintains a decreased hardness when subsequently held at lower temperatures. To determine whether a reduction in solid fat content occurs when pure butterfat is similarly treated, September butterfat was cooled by immersion of the dilatometers in a 0°C. waterbath, subsequently stored at 22.5°C. for 1 week and finally

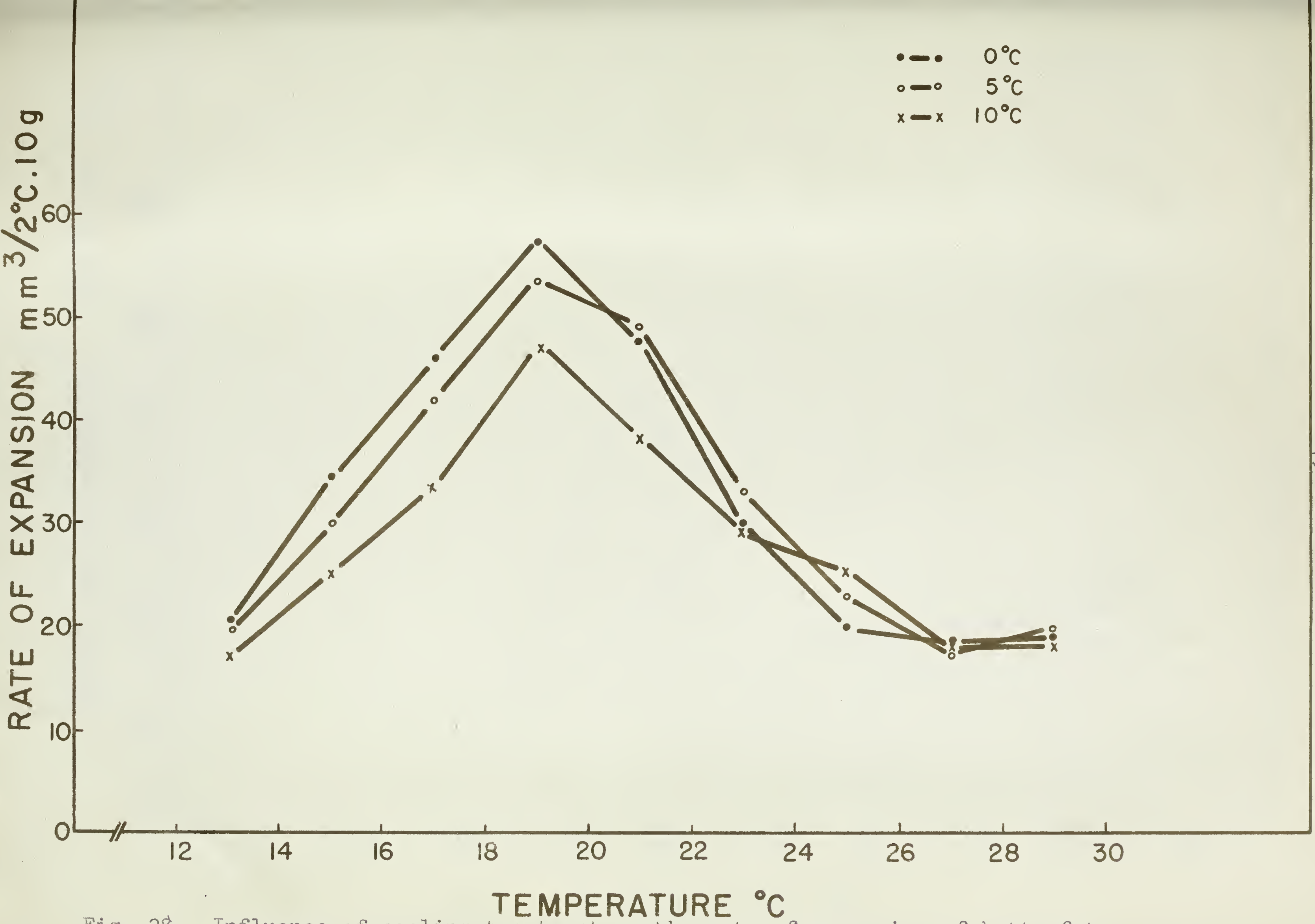


Fig. 28. Influence of cooling treatment on the rate of expansion of butterfat

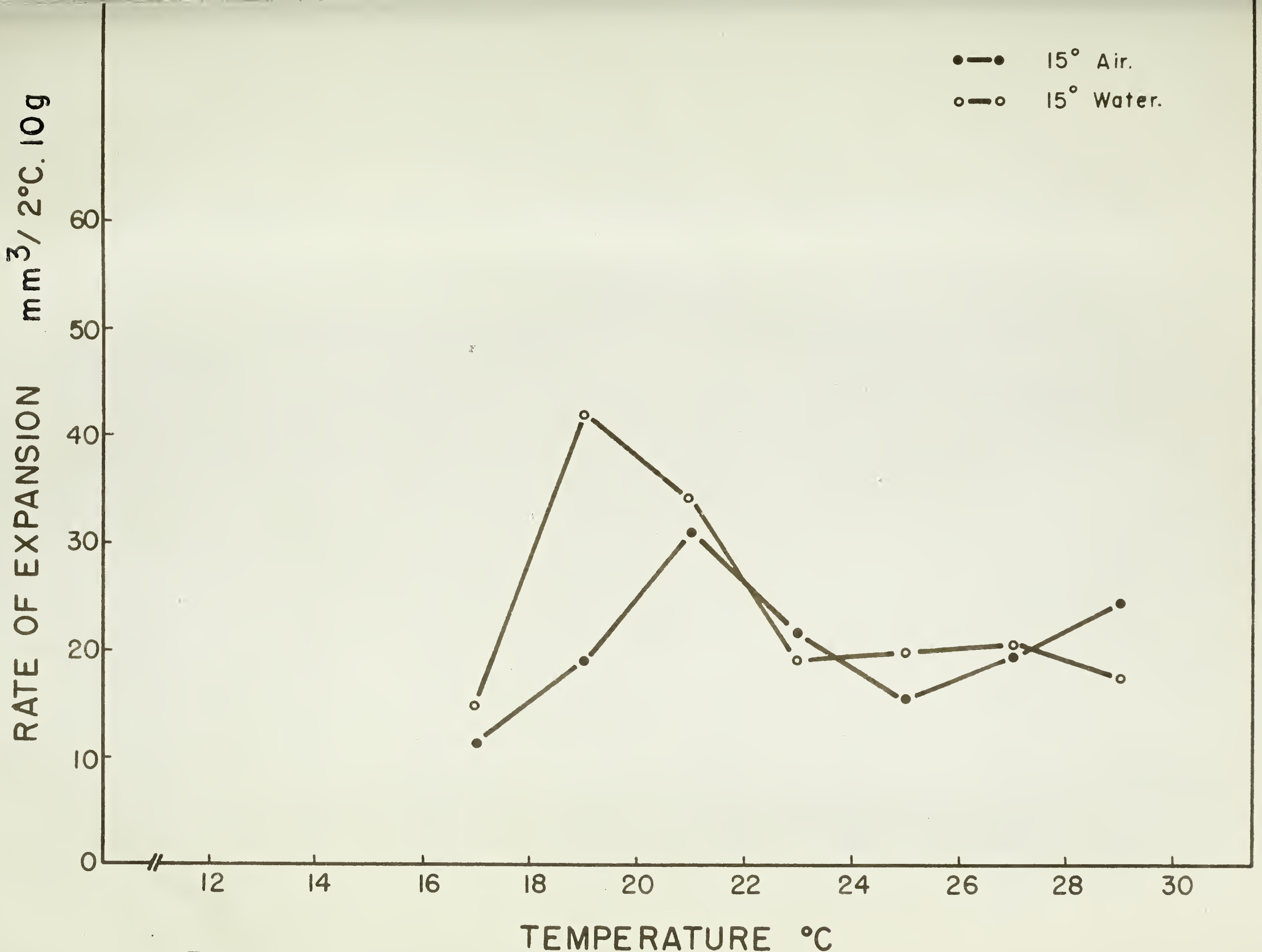


Fig. 29. Influence of cooling treatment on the rate of expansion of butterfat

Table 13. Influence of season on the percentage of solid phase in butterfat

Measurement temperature °C.	Solid fat %					
	Dilatometers cooled in water at 0°C.			Dilatometers cooled in air at 15°C.		
	June	September	December	June	September	December
12	52	56	64	-	-	-
14	48	53	61	-	-	-
16	42	47	56	27	29	36
18	33	39	49	26	27	33
20	25	30	39	23	24	30
22	18	23	30	18	19	24
24	14	18	23	15	16	20
26	11	15	18	10	13	17
28	9	12	15	8	10	15
30	6	9	12	5	7	13

kept overnight at 5°C. A definite reduction in solid fat content was obtained as shown in table 14.

Calorimetry. Purified butterfats obtained from butters produced in June and December were melted and weighed into aluminum cans. The cans were then tempered either in water at 0°C. (rapid cooling) or in an air incubator at 15°C. (slow cooling). The rapidly cooled samples were removed from the 0°C. waterbath after 2 hours and then stored overnight at 15°C. before measurement. The heat required to melt the fat present in the crystalline state at 15°C. was calculated by using a specific heat value for butterfat of 0.52 cal/g (84). Measurements were also made with continuously made and conventional butters produced in June and December. For the calculation of the heat of fusion of the crystalline fat portion in butter, the specific heat of the butter serum was taken as 0.95 cal/g (84). Results of these measurements are listed in table 15. More heat was required to melt the crystalline portion of rapidly cooled fat than that of slowly cooled fat, irrespective of whether the fat was produced from June or December butter. Similarly more heat was required to melt the crystalline portion of the fat in continuously made butter than that of

Table 14. Influence of storage at 22.5°C. on the percentage of solid phase in September butterfat

Measurement temperature	Solid fat %	
	Before storage at 22.5°C. [a]	After storage at 22.5°C. [b]
(°C.)		
12	56	45
14	53	40
16	47	35
18	39	29
20	30	22
22	23	17
24	18	16
26	15	14
28	12	12
30	9	10

[a] Dilatometers cooled in water at 0°C.

[b] After cooling in water at 0°C., dilatometers were stored for 7 days at 22.5°C. and cooled in a refrigerator at 5°C. for 12 hr.

Table 15. Average heat of fusion of butterfat and butter between 15° and 55°C.

Sample and treatment	Calories required to melt the crystalline fraction in one gram of fat	
	June	December
butterfat(slow cooling)	9.2	9.5
butterfat(rapid cooling)	13.0	13.3
butter(conventional)	10.0	10.2
butter(continuous)	12.7	12.8

conventional butter produced in the same season. However, no such differences were found between butterfats and butters of different seasons. While there is thus an indication of different crystal contents in butterfats cooled at different rates, this technique would appear to give no indication of different crystal contents in fats of different seasons.

DISCUSSION

Structure. Contrary to an assertion in the literature (107) that conventional and continuously made butters possess identical crystal structure, it was found that crystal form, size and arrangement in continuously made butter are characteristic and different from conventional butter. The realization that in the continuous method the melted butterfat is subjected to very rapid cooling and violent agitation made the occurrence of the relatively large crystal masses an unexpected finding, especially after it was found that rapid cooling ordinarily produces very small crystals in butterfat. Some special condition of the process must be responsible for this phenomenon, and this will be discussed in more detail in the section on crystallization.

The absence of globular fat in continuously made butter is an indication that the disruption of fat globule membranes and the subsequent separation of fat and water phases are practically complete in

the cream destabilization step of the process.

The photomicrographs of summer and winter butters gave an indication that differences in crystalline fat content may play an important role in determining physical properties of butter. This was to be expected as a study of chemical and physical properties of Alberta butterfat (113) had already given evidence of considerable seasonal variations in these properties.

The finer moisture distribution in the continuously made butter is undoubtedly a result of the intensive working and agitation applied in this process. As a result of this finer moisture distribution the continuously made butter never shows the defect of "free moisture" or "leakiness" which frequently occurs in conventional butter (5, 77, 78, 96).

Hardness. As butter is mainly used as a spread its rheological behaviour has received a great deal of attention. A large number of methods and instruments has been used for measuring the rheological properties of butter (14, 50, 57, 59, 61, 67, 82, 86, 87, 112), but, unfortunately, there is uniformity

neither in terminology nor in interpretation of results. While it has become clear that a detailed knowledge of the physical structure will enable us to understand and influence the rheological behaviour of butter, there is still much confusion re the connection between structure and properties in the case of conventional butter and a nearly complete lack of information in the case of continuously made butter.

Some of the rheological methods proposed for the study of butter were adapted to the determination of exact physical properties, e.g., viscosity (14, 67, 97); others have been linked to subjective assessments (50, 86). Hardness of butter is usually measured within the range of 12° - 17°C., and in choosing measurement temperatures the important consideration is that the range of hardness values encountered falls within the range of the particular instrument used. By using the methods as described earlier all samples could be measured by the penetrometer method at 17°C. or by the sectility method at 12°C.

The meaning of the term spreadability, which is frequently used, is rather vague, and some

investigators are of the opinion that spreadability and hardness are not directly related (86, 105), whereas, on the other hand, the most widely used methods for the determination of rheological behaviour of butter are of the sectility and penetrometer types. Recent work (31) has established a highly significant correlation between spreadability and hardness as determined by a sectility method. In the present work a highly significant correlation was obtained between sectility and penetrometer techniques. It seems likely, therefore, that all these methods measure essentially the same property of butter. Hardness has been defined as "a measure of the resistance to permanent deformation or damage" (68). If this definition is accepted, penetrometer, sectility, spreadability, and other methods are all fundamentally hardness measurements, although the results are not always directly comparable.

The hardness of butter made by the continuous method, by comparison of corresponding weekly samples, was always significantly higher than that of conventional butter. As the seasonal changes in the two butter types were similar, the increased

hardness of the continuously made butter is clearly the result of features which are peculiar to the process and which result in a permanent effect on the physical structure of that butter.

It is to be noted that the penetrometer hardness differences between the two butters do not reach the magnitude of differences caused by inherent seasonal variations. Dolby (15) estimated that up to 80% of the differences in hardness of conventional butter were caused by seasonal variations in the composition of the butterfat. As was indicated in the review of the literature, considerable interest has been shown in attempts to influence rheological properties of conventional butter by variation in temperature treatments of cream and butter. The continuous method undoubtedly represents an extreme treatment, as the fat is subjected to rapid cooling and agitation in the chilling compartment, but the resulting penetrometer hardness changes are still of lower magnitude than the seasonal differences.

The finding that conventional and continuously made butters with identical hardness when measured at 17°C. are of different hardness when measured at 12°C. indicates that temperature changes have a

different effect on the crystal conditions in the two butter types. This is of particular significance in connection with oiling-off properties of butter and the formation of mixed crystals. The formation of mixed crystals (solid solutions) involves the inclusion of lower melting glycerides in the crystal lattice of a particular glyceride. This phenomenon will be favored in fats with a complicated fatty acid and glyceride composition. Since butterfat has the largest number of different component fatty acids and glycerides of all natural fats, conditions are ideal for mixed crystal formation. Mixed crystal formation will lead to an increased content of crystalline phase when compared with a fat in which no mixed crystals are present. The increased hardness of continuously made butter may, therefore, be partly the result of a higher crystalline fat content.

Oiling-off. The oiling-off tendency is an indication of the amount of free liquid fat in the butter, as well as of the character of the structure binding the liquid portion of the fat. It may be expected, e.g., that more liquid fat would drain from a fat

containing coarse crystals than from a fat with fine crystals. The fact that in conventional butter part of the liquid fat is present inside the globules and thus not available for drainage should also influence the oiling-off tendency.

Oiling-off properties may be expected to vary with the composition of the butterfat, which is subject to considerable seasonal change. According to Hilditch (30) the glycerides in butterfat are of three general types, viz., (1) trisaturated, (2) monounsaturated-disaturated, and (3) diunsaturated-monosaturated. Seasonal differences in composition of butterfat involve mainly types 1 and 3, whereas type 2 remains fairly constant. As type 3 glycerides are those with the lowest melting point, it is not surprising to find the seasonal variation in oiling-off as pronounced as was demonstrated.

The presence of mixed crystals may be of importance as a factor influencing oiling-off. Mixed crystal formation is a phenomenon commonly encountered with lipid mixtures (25, 36, 49). It has been stated (63) that rapidly cooled fat forms crystals which have a lower melting point than those

of a fat cooled more slowly. If considerable mixed crystal formation occurs in the manufacture of continuously made butter a higher than normal proportion of crystals will melt at 25°C, resulting in increased oiling-off.

Variations in the disperse phase. The results of the experiments in which varying amounts of gas were incorporated into continuous type butter indicate that gas content may be an important factor influencing butter hardness. While the development of the experimental continuous buttermaking machine made possible the addition of gas at different levels, it is, unfortunately, not yet possible to influence the size of the gas bubbles. The results obtained in this way, therefore, are only applicable to continuously made butter and cannot serve in a comparison of continuously made and conventional butters. The gas present in conventional butter is not as finely divided as it is in continuously made butter and may thus exert a lesser influence on the rheological behaviour of the butter. Recently, with the introduction of metal vacuum churns it has become possible to manufacture butter of a lower than normal gas content. Reports on the effect of the lowering

of the gas content on the hardness of such butter are contradictory as was indicated in the review of the literature. While it is not yet possible to determine to what extent the differing gas contents of the two butter types are involved in the hardness differences, it must be assumed that at least to some extent the greater hardness of continuously made butter is a result of its low gas content.

Continuous type butters with varying proportions of globular fat had a remarkably uniform hardness. All of these butters were much harder than the conventional butter made from the same ingredients. Apparently, the presence of globular fat is of no consequence as far as hardness of continuously made butter is concerned. These experiments show that the cooling procedure is of paramount importance in determining the nature of the structure and properties of continuously made butter and especially the condition of the fat phase. Mulder (70), in studying conventional butter, stated that its consistency is mainly determined by the condition of the fat phase in it. This applies equally well for continuously made butter.

Setting. In the study of the rheological properties of butter much interest has been shown in that part of the buttermaking process that deals with temperature treatment of the cream and the churning itself. Interest in the setting phenomenon, however, has been relatively limited. This is surprising, because, as a result of the important changes that may take place, the final properties of butter are to an important extent determined by setting. It is obvious that the measurement of rheological constants shortly after manufacture is only of value for the purpose of comparisons when time and temperature of storage are standardized, as butter during the first few days after manufacture is ordinarily in a state of rapid change.

The experiment in which butters were held at a constant temperature equal to that prevailing at the conclusion of the manufacturing process showed that continued crystallization cannot be the only and most important cause of setting in conventional butter. It follows from the absence of any temperature rise in conventional butter stored in Dewar flasks after

manufacture that no measurable crystallization occurs. The setting in conventional butter, therefore, is definitely not connected with continued crystallization. In the continuously made butter, on the other hand, a temperature increase under these conditions indicates that crystallization is in progress during a period of several hours after manufacture. In this case the hardness increase must be attributed, at least partially, to continued crystallization.

The extent to which thixotropy may occur is dependent on the composition of the system and the characteristics of the dispersed particles and the continuous phase. Whereas crystallization is accompanied by a considerable evolution of heat, the sol-gel transformation does not involve any measurable heat effect.

Dispersed particles can be classified as spherical (isometric) or non-spherical (anisometric). Thixotropy may be produced by particles of various shapes, but as a rule anisometric particles show more pronounced thixotropy (88). It is generally agreed that thixotropy will not take place when dispersed particles exceed a certain size limit

and a maximum of one micron has been suggested (88).

The water droplets and fat globules in butter are isometric and a large proportion of these exceed one micron in size. They will thus not likely be involved in thixotropic changes. The fat crystals in the free fat of conventional butter are anisometric and mostly under one micron in size. These crystals are, therefore, of the size, shape and quantity favourable for the occurrence of thixotropy. It is highly probable that the small needle-shaped fat crystals have a far greater influence on the thixotropy of butter than have the remaining, mostly isometric, particles.

In the production of continuously made butter in which the fat is present in free (i.e., non-globular) form during the cooling stage, relatively large crystals are formed. The presence of fewer fat crystals of extremely small size in continuously made butter may explain the lower magnitude of the setting of this butter as compared with conventional butter. The influence of the quantity of crystals is also seen in the

setting of summer and winter butters. Summer butters with less crystalline fat show a lower extent of setting than winter butters with higher crystalline fat contents.

When butter is worked as in printing, it is usually appreciably lowered in hardness. The hardness increases again on storage, but does not reach the original value. Thixotropy does not explain this lack of complete reversibility. In order to understand this it is well to realize that dispersed particles of various kinds make up two thirds of the total volume of butter. It is evident that in such a system an interaction between a considerable number of the dispersed particles must exist, independently of thixotropy. It is proposed to name the structure that is built up from the larger particles the primary structure. Its contributing elements, because of their relatively large size, cannot be expected to possess freedom of movement. The primary structure would thus not contribute to thixotropic changes in the butter. The small particles in the interstices between the larger particles possess a certain freedom of movement and by their rearrangement could add to and reinforce the

primary structure. This structure may be named the secondary structure and is formed as the result of thixotropy. It is evident that primary and secondary structures are intimately connected and that any disturbance of the butter by mechanical treatment will affect both the primary and the secondary structures. On working butter the secondary structure may be disturbed and subsequently reformed on storage, but the primary structure may have been damaged permanently. In this way the lack of complete reversibility during setting can be explained.

The effect of storage temperature on setting provides further evidence for the contention that thixotropy is involved in setting. Storage at -20°C. completely prevented setting, but it was resumed immediately after removal to a higher temperature storage. At -20°C. the fat in butter is nearly completely solidified and under these conditions any movement of crystals and rearrangement of structure is prevented. As soon as sufficient fat is liquified at a higher temperature the process of structure formation continues. It is thus possible to interrupt setting

at any desired stage and for any desired length of time merely by storage at freezer temperature. There is apparently an optimum temperature for setting because at 15°C. there was less setting than at 5°C. This may also have to do with the quantities of crystalline fat present at different temperatures.

Crystallization. The state of dispersion and relative quantity of the crystalline portion of the fat is possibly the most important factor determining the properties of butter. While in conventional butter the crystallization process is practically complete at churning, crystallization occurs during and after the manufacturing process in continuously made butter. When the fat-serum mixture enters the chiller in the continuous process it is cooled from 40°C. to about 0°C. and the holding time in this part of the equipment is approximately two minutes. Crystallization of the fat is far from complete at this stage as is indicated by the fact that the butter after leaving the chiller and held under adiabatic conditions may show a temperature increase of up to 10°C. If the value of 0.52 cal/g is taken for specific heat of the fat and 20 cal/g for the heat of crystallization (34), then a simple

calculation reveals that about 26% of the fat crystallizes after emerging from the chiller. As the butterfat at the final temperature does not contain much over 50% of crystallized fat, only about half of the crystallization occurs in the chiller. This explains the presence of relatively large crystals in continuously made butter in spite of the rapid cooling and violent agitation in the chiller. The fat crystals, once formed in the chiller, move into the texturator where little agitation is provided and conditions are ideal for further growth.

Besides the size of the fat crystals, the ratio of solid to liquid butterfat is an important factor in determining butter hardness. It has been known for many years that winter butter is much harder than summer butter, and there is no doubt that variations in the chemical composition of the fat are mainly responsible. These variables include unsaturated and short chain fatty acids (10, 11, 81, 98, 113, 114), glyceride composition (22, 23), and possibly the occurrence of relatively large quantities of trans-fatty acids (6, 28, 103). The dilatometric measurements on pure butterfats resulted in

maximum, intermediate and minimum solid fat content values for December, September and June butterfats respectively, both for rapid and slow cooling. Seasonal differences in the solid fat content, therefore, parallel the differences in the hardness of the butter. The influence of variations in the cooling rate was studied on September fat and very marked differences in solid fat content were found. Higher cooling rates, obtained by immersion of the dilatometers in coolants of lower temperatures, increased the solid fat content and the increases were most apparent at the lower measuring temperatures. It must be assumed that more rapid cooling resulted in the formation of mixed crystals. The fact that there was practically no difference between the values obtained by cooling to 5° and 0°C. indicates that maximum mixed crystal formation occurs at about 5°C. It is, therefore, unlikely that a further increase in solid fat content can be obtained with still higher cooling rates (lower cooling temperatures or increased agitation).

Mixed crystals will contain glycerides of different melting points and a rapidly cooled fat will have a lower melting point than the same fat which is

cooled slowly (27). Since the maximum melting of the rapidly chilled butterfat was between 18° and 20°C., but between 20° and 22°C. in the slowly cooled fat, the melting point of the fat in continuously made butter is lower than that of conventional butter. The greater oiling-off tendency of continuously made butter may be partly the result of this difference in melting points. The difference in crystal composition in the two butters can also serve to explain the different results obtained when the hardness of the two butters measured at different temperatures is compared. The continuously made butter containing the mixed crystals would be expected to get softer more quickly when temperatures are increased because more fat would melt at any one temperature.

The variations in solid fat contents resulting from the seasonal and cooling treatment differences are of a different character. The seasonal differences indicate relatively large variations in the higher melting glycerides, whereas the cooling treatment variations occur mainly at the lower measuring temperatures, indicating an increase in lower melting-point crystals. It is possible that

these two types of crystals may not be equal in their relative effect on butter hardness. It has been pointed out (4) that crystals composed in large part of high melting glycerides possess more rigidity and greater stiffening power than crystals of lower melting glycerides. Very slow cooling would result in a minimum of crystalline fat and the crystals would have a relatively sharp melting point. It is not likely that this ideal situation will occur in butter made by the conventional method. It must rather be assumed that with that type of butter mixed crystal formation also occurs, though to a much lesser extent than in the continuous process. Evidence in favor of this assumption is obtained from the microscopic study of butters stored at 22.5°C. In both butter types a reduction of crystalline fat was observed that can only be explained by assuming the recrystallization of mixed crystals resulting in a lower solid fat content. This was confirmed by dilatometric measurement of similarly treated fats. It is interesting to observe that, after high temperature storage, butters of both types had approximately the same hardness.

The calorimetric measurements confirmed that

rapid cooling results in more crystalline fat than slow cooling. This was found not only to be true for pure butterfats but to hold also for butter, as more heat was required to melt continuously made than conventional butter. It is remarkable therefore that no difference was found in heat of fusion between summer and winter butterfats and butters. While it has been reported in one calorimetric study (92) that such differences were indeed observed, a more recent report (90) shows very little difference in heat content of summer and winter butterfat over a very wide temperature range. In a calorimetric study of the fat in cream (84) it was stated that the influence of seasonal variations in heat content of butterfat is likely to be small. There is, however, ample evidence, obtained from microscopic study, dilatometry, hardness measurements and measurements of chemical and physical constants, to indicate that winter butterfat should contain more crystalline fat at any specified temperature than summer fat at the same temperature. Yet no difference is found by calorimetric measurements. The reason for this apparent anomaly is unknown and it must be assumed that the glycerides of differing composition and structure that are found in these butterfats have widely

varying thermal properties.

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